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THE

PHYSICAL REVIEW

THE PENETRATION OF A POTENTIAL BARRIER BY ELECTRONS

By Carl Eckart

Ryerson Physical Laboratory, University of Chicago

(Received April 21, 1930)

Abstract

A potential barrier of the kind studied by Fowler and others may be represented by the analytic function V (Eq. (1)). The Schrödinger equation associated to this potential is soluble in terms of hypergeometric functions, and the coefficient of reflection for electrons approaching the barrier with energy W is calculable (Eq. (15)). The approximate formula,

$$1-\rho=\exp\left\{-\int\frac{4\pi}{h}(2m(V-W))^{1/2}dx\right\}$$

is shown to agree very well with the exact formula when the width of the barrier is great compared to the de Broglie wave-length of the incident electron, and $W<V_{max}$.

THE "failure" of the law of conservation of energy in quantum dynamics, as evidenced by the penetration of an electron through a region of space in which its potential energy is greater than its total energy, has been advanced as the explanation of several phenomena. Gamow,[1] Gurney and Condon,[2] and others have discussed it in relation to the Geiger-Nuttall law of the radioactive decay constants; Fowler and Nordheim[3] in its relation to the lowering of the thermionic work-function by surface impurities, and to the emission of electrons from cold metals under the influence of strong fields.

The mathematical discussions in these papers have all been based either on a potential function which has discontinuous derivatives, or else on approximate treatments involving asymptotic (i.e., divergent) series. It is therefore of some interest to note that there is an analytic function which represents some of the types of potential barriers which have been discussed and whose associated Schrödinger equation is soluble. This function is

$$V(x) = -A\xi/(1-\xi) - B\xi/(1-\xi)^2, \quad \xi = -\exp(2\pi x/l), \tag{1}$$

[1] G. Gamow, Zeits. f. Physik **51,** 204 (1928).

[2] R. W. Gurney and E. U. Condon, Phys. Rev. **33,** 127 (1929).

[3] R. H. Fowler, Proc. Roy. Soc. **A122,** 36 (1929), **A117,** 549 (1927). L. Nordheim, Zeits. f. Physik **46,** 833 (1928).

in which x is the cartesian coordinate, and A, B, and l are constants. The graphs of this function for various values of A and B are shown in Fig. 1. It is seen to approach zero for large negative values of x and a constant value

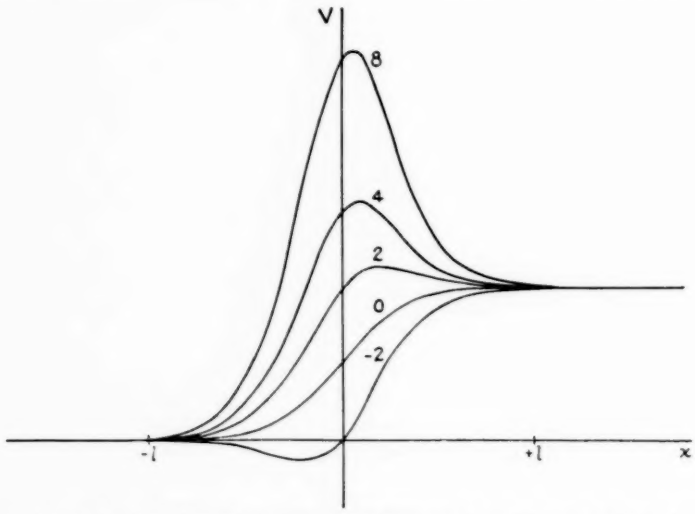

Fig. 1. Graphs of the function $V(x)$. The numbers on the curves are the values of B/A.

A for large positive values. The width of the transition region is, practically speaking, $2l$. When $|B|$ is greater than $|A|$ it possesses an extremum at

$$x_m = \frac{l}{2\pi} \log \left[(B + A)/(B - A)\right],$$

whose height is

$$V(x_m) = V_m = (A + B)^2/4B. \tag{2}$$

In the following, it will be assumed that $B \geqq 0$ so that the extremum is a maximum, when it exists at all.

The wave equation governing the dynamical problem of an electron moving under the action of this potential is

$$\frac{d^2u}{dx^2} + \frac{8\pi^2 m}{h^2}\{A\xi/(1 - \xi) + B\xi/(1 - \xi)^2 + W\}u = 0 \tag{3}$$

or if differentiation with respect to ξ be indicated by an accent

$$\xi^2 u'' + \xi u' + \frac{2ml^2}{h^2}\{A\xi/(1 - \xi) + B\xi/(1 - \xi)^2 + W\}u = 0. \tag{4}$$

This equation[4] is of the hypergeometric type, and its solutions may therefore be written down at once in terms of the hypergeometric series:[5]

[4] Special cases ($A = 0$, and $B = 0$) of this equation were discussed in the Colloquium at Pasadena by Professor P. Epstein in 1925, the occasion being the work of Epstein and Robertson on the reflection of radio waves by the Heaviside layer.

[5] F. Klein, Ueber die hypergeometrischen Reihen, (Göttingen, 1894) pp. 3–7. A. R. Forsythe, Treatise on Differential Equations, (2d, one vol. ed.) (New York, 1888) p. 185.

$$F(a,b,c,y) = 1 + \frac{a\cdot b}{1\cdot c}y + \frac{a(a+1)\cdot b(b+1)}{1\cdot 2\cdot c(c+1)}y^2 + \cdots . \tag{5}$$

Before proceeding to study the exact solutions, it will be well to consider their asymptotic behavior for very large positive and negative values of x. In both cases, the potential is practically constant and therefore the solutions should be monochromatic de Broglie waves to a first approximation. For large negative values of x the wave-length will be $\lambda = h/(2mW)^{1/2}$, for large positive values, $\lambda' = h/(2m(W-A))^{1/2}$. It may be assumed that $W \geqq A$, since the interest in the other case is not very great. The solution may be specified even more precisely if we confine ourselves to the case in which the electrons are incident on the barrier from $x = -\infty$. Then there will be a single (transmitted) wave

$$\exp(2\pi i x/\lambda') = (-\xi)^{i\beta}, \quad \beta = l/\lambda' \tag{6}$$

for large positive values of x, and two waves (incident and reflected) for large negative values of x:

$$a_1 \exp(2\pi i x/\lambda) + a_2 \exp(-2\pi i x/\lambda) = a_1(-\xi)^{i\alpha} + a_2(-\xi)^{-i\alpha}, \ \alpha = l/\lambda. \tag{7}$$

As will be shown, the condition that the exact solution reduce approximately to these values for large values of x, suffices to determine it uniquely, and also to determine the constants a_1 and a_2. The quantity $\rho = |a_2/a_1|^2$ is the reflection coefficient, whose value is required for the applications mentioned in the first paragraph.

In working with the hypergeometric series, Eq. (5), it must be borne in mind that it converges only for $|y| < 1$. It then appears that of the twenty-four well-known ways[6] in which solutions of the hypergeometric equation can be expressed in terms of $F(a, b, c, y)$, only eight converge for large values of ξ $(x > 1)$; of these only four approach $(-\xi)^{i\beta}$ (the other four approaching $(-\xi)^{-i\beta}$) when $|\xi|$ increases indefinitely. The four solutions approaching $(-\xi)^{i\beta}$ are only formally different, so that it suffices to study any one of them; we single out the form

$$u = (1-\xi)^{i\beta}(\xi/\xi - 1)^{i\alpha} F[\tfrac{1}{2} + i(\alpha - \beta + \delta), \\ -\tfrac{1}{2} + i(\alpha - \beta - \delta), \ 1 - 2i\beta, \ 1/(1-\xi)] \tag{8}$$

in which α and β have the values of Eqs. (6) and (7) and δ is to be defined immediately. If we define a quantity C by the relation $(2mC)^{1/2} = h/2l$, it becomes possible to write

$$\alpha = \tfrac{1}{2}(W/C)^{1/2}, \quad \beta = \tfrac{1}{2}[(W-A)/C]^{1/2}, \tag{9}$$

and the quantity δ is then defined by

$$\delta = \tfrac{1}{2}[(B-C)/C]^{1/2}. \tag{9a}$$

[6] Klein, pp. 76–80; Forsythe, pp. 189–194.

C is the energy of an electron whose de Broglie wave-length is $2l$, the total width of the region of variable potential.

The function u of Eq. (8) obviously approaches $(-\xi)^{i\beta}$ for large values of ξ, since $F(a, b, c, o) = 1$. Its value for very small values of ξ cannot be determined at once, however, since the series $F(a, b, c, 1)$ diverges. It is necessary to have recourse to the so-called process of analytic extension, and to express u in terms of series which do converge for small values of $|\xi|$. The result of the analytic extension of the hypergeometric series has been known, practically speaking, since the times of Euler and Gauss; it is summarized in the formula[7] for compounding two hypergeometric series:

$$\begin{aligned} y^{a}(1-y)^{c}F(a+b+c,\ a+b'+c,\ 1+a-a',\ y) \\ = \phi(c,c')(1-y)^{c}y^{a}F(a+b+c,\ a+b'+c,\ 1+c-c',\ 1-y) \\ + \phi(c',c)(1-y)^{c'}y^{a}F(a+b+c',\ a+b'+c',\ 1+c'-c,\ 1-y) \end{aligned} \tag{10}$$

where

$$\phi(c,c') = \frac{\Gamma(1+a-a')\Gamma(c'-c)}{\Gamma(1-a'-b-c)\Gamma(-a'-b'-c)}. \tag{11}$$

This equation is an identity for those values of y for which all the series converge, and may be used as a definition of $F(a, b, c, y)$ for $|y|>1$, $|1-y|<1$. If we set y equal to $1/(1-\xi)$, $a=-a'=-i\beta$, $b=-b'=\frac{1}{2}+i\delta$, $c=-c'=i\alpha$, and

$$\begin{aligned} a_1 &= \frac{\Gamma(1-2i\beta)\Gamma(-2i\alpha)}{\Gamma[\tfrac{1}{2}+i(-\alpha-\beta-\delta)]\Gamma[\tfrac{1}{2}+i(-\alpha-\beta+\delta)]}, \\ a_2 &= \frac{\Gamma(1-2i\beta)\Gamma(+2i\alpha)}{\Gamma[\tfrac{1}{2}+i(\alpha-\beta-\delta)]\Gamma[\tfrac{1}{2}+i(\alpha-\beta+\delta)]}, \end{aligned} \tag{12}$$

it reduces to

$$\begin{aligned} u = a_1(\xi/\xi-1)^{i\alpha}(1-\xi)^{i\beta}F[\tfrac{1}{2}+i(\alpha-\beta+\delta), \\ -\tfrac{1}{2}+i(\alpha-\beta-\delta),\ 1+2i\alpha,\ \xi/(\xi-1)] \\ + a_2(\xi/\xi-1)^{-i\alpha}(1-\xi)^{i\beta}F[\tfrac{1}{2}+i(-\alpha-\beta+\delta), \\ -\tfrac{1}{2}+i(-\alpha-\beta-\delta),\ 1-2i\alpha,\ \xi/(\xi-1)]. \end{aligned} \tag{13}$$

The two series on the right side of this equation converge when $|\xi/(\xi-1)|<1$ hence certainly when $|\xi|<\frac{1}{2}$. For very small values of ξ the value of u may be computed from this equation, and is seen to be exactly the expression of Eq. (7) with a_1 and a_2 defined by Eqs. (12). Eqs. (8) and (13) thus define the function u for all real values of x; it may readily be shown that it satisfies[8] Eq. (4), and is finite, continuous, and possesses continuous derivatives

[7] Klein, pp. 88–91; Forsythe, pp. 194–201.

[8] For it is a linear function of two of Kummer's twenty-four solutions (cf. reference 6).

throughout this range. It is therefore the wave-function we are seeking, and the coefficient of reflection is hence

$$\rho = \left|\frac{a_2}{a_1}\right|^2 = \left|\frac{\Gamma[\frac{1}{2} + i(\delta - \beta - \alpha)]\Gamma[\frac{1}{2} + i(-\delta - \beta - \alpha)]}{\Gamma[\frac{1}{2} + i(\delta - \beta + \alpha)]\Gamma[\frac{1}{2} + i(-\delta - \beta + \alpha)]}\right|^2 \tag{14}$$

since $|\Gamma(2i\alpha)/\Gamma(-2i\alpha)|$ is obviously 1.

In the numerical evaluation of this formula the two cases, δ = real and δ = imaginary, are to be distinguished. These two cases are separated by the condition $B = C$; since B will in general be of the order of magnitude of W, the case of a real δ corresponds to a potential barrier whose region of inhomogeniety is wide compared to the wave-length of the incident electron (cf. Eq. (9)) while an imaginary δ corresponds to a narrow region of inhomogeniety.

If δ is real, the arguments of all the gamma-functions have the form $\frac{1}{2} + iv$, where v is real. It is known that[9]

$$|\Gamma(u + iv)| = \Gamma(u) \exp[-P(u,v)]$$

and that

$$\exp[P(\tfrac{1}{2}, v)] = [\cosh(\pi v)]^{1/2}.$$

Hence

$$\begin{aligned}\rho &= \frac{\cosh[\pi(\delta - \beta + \alpha)]\cosh[\pi(\delta + \beta - \alpha)]}{\cosh[\pi(\delta - \beta - \alpha)]\cosh[\pi(\delta + \beta + \alpha)]} \\ &= \frac{\cosh[2\pi(\alpha - \beta)] + \cosh[2\pi\delta]}{\cosh[2\pi(\alpha + \beta)] + \cosh[2\pi\delta]}.\end{aligned} \tag{15}$$

If δ is imaginary, both the numerator and denominator of Eq. (14) have the form

$$|\Gamma(u + iv)\Gamma(1 - u + iv)|$$

with $u = \frac{1}{2} + |\delta|$. Now,

$$\exp[P(u,v) + P(1 - u,v)] = [(\cosh 2\pi v - \cos 2\pi u)/2 \sin^2 \pi u]^{1/2}$$

and hence

$$\rho = \frac{\cosh[2\pi(\alpha - \beta)] + \cos[2\pi|\delta|]}{\cosh[2\pi(\alpha + \beta)] + \cos[2\pi|\delta|]}. \tag{15a}$$

The two Eqs. (15) and (15a) are identical, if it be remembered that

$$\cosh[2\pi\delta] = \cos[2\pi|\delta|]$$

[9] The formulae regarding $\Gamma(u+iv)$ which are used in the following are all to be found on pp. 23–25 of N. Nielsen, Handbuch der gammafunktion, (Leipzig, 1906).

when δ is imaginary; the separate derivation of the two is necessary, however, for $|\Gamma(u+iv)|$ is not an analytic function. The expressions for ρ are plotted in Fig. 2 for $B=8A$ and various values of l.

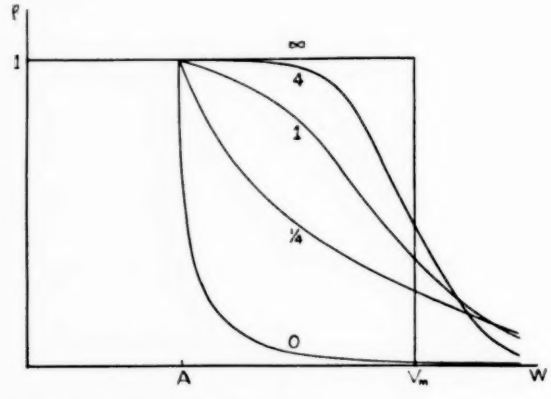

Fig. 2. Graphs of the reflection coefficient. The numbers are the values of A/C.

It is instructive to compare this expression for the reflection coefficient with the values which have been obtained by other writers. If $W<V_m$, the expression

$$1-\rho=\gamma\exp\left\{-\frac{4\pi}{h}\int(2m(V-W))^{1/2}dx\right\} \tag{16}$$

has been used, in which the integral is to be extended over all values of x for which $V>W$, and $\gamma\sim 1$. It may be shown that this is a valid approximation to Eq. (15) when l is very large, C very small. In this case, α and β become very large, so that

$$\cosh\left[2\pi(\alpha\pm\beta)\right]\sim\tfrac{1}{2}\exp\left[2\pi(\alpha\pm\beta)\right]$$

and $\delta\sim\frac{1}{2}(B/C)^{1/2}$. Hence, approximately,

$$\rho=\frac{1+\exp\left[\pi(W^{1/2}-(W-A)^{1/2}-B^{1/2})/C^{1/2}\right]}{1+\exp\left[\pi(W^{1/2}+(W-A)^{1/2}-B^{1/2})/C^{1/2}\right]}.$$

The argument of the exponential in the denominator of this expression is very much greater than 1 when $W\gg V_m$, and very much less than -1 when $W\ll V_m$. Hence

$$\rho=\exp\left[-\pi(W^{1/2}+(W-A)^{1/2}-B^{1/2})/C^{1/2}\right[\tag{17}$$

when $W\gg V_m$, and

$$(1-\rho)=\left\{1-\exp\left[-2\pi((W-A)/C)^{1/2}\right]\right\}\exp\left[\pi(W^{1/2}+(W-A)^{1/2}-B^{1/2})/C^{1/2}\right]$$

when $W \ll V_m$. When l is very large, therefore, ρ is practically zero if $W > V_m$ and practically 1 if $W < V_m$; these formulae are valid except when $|W - V_m| \sim C$. Comparing the second of Eqs. (17) with Eq. (16) it is seen that the latter is verified if

$$-\frac{4\pi}{h}\int (2m(V-W))^{1/2}dx = \pi(W^{1/2} + (W-A)^{1/2} - B^{1/2})/C^{1/2}.$$

The integral on the left is readily evaluated by the method of residues,[10] and does prove to be equal to the right side of the equation.

For very small values of l (C very large) $\cosh 2\pi\delta$ approaches -1 regardless of B and

$$\cosh 2\pi(\alpha \pm \beta) = 1 + \pi^2[W^{1/2} \pm (W-A)^{1/2}]^2/8C$$

so that

$$\rho = [W^{1/2} - (W-A)^{1/2}]^2/[W^{1/2} + (W-A)^{1/2}]^2.$$

In this limit, therefore, all effect of the maximum of potential function vanishes and the reflection coefficient has the value characteristic of a rectangular potential barrier of infinite width,[11] and height A.

For values of W very much larger than A, B, or C,

$$\cosh[2\pi(\alpha-\beta)] \sim 1, \quad \cosh[2\pi(\alpha+\beta)] \sim \tfrac{1}{2}\exp[2\pi(W/C)^{1/2}],$$

so that

$$\rho = [1 + 2\cosh(2\pi\delta)]\exp[-2\pi(W/C)^{1/2}].$$

For $W \leqq A$ the reflection coefficient is always unity, as may be most readily deduced from general principles.

[10] See, e.g., A. Sommerfeld, Atombau, (4th Ed. 1924), p. 772.

[11] See, e.g., W. Heisenberg, Physical Principles of the Quantum Theory (in course of publication.)

THE QUANTUM MECHANICS OF ELECTRONS IN CRYSTALS

By Philip M. Morse
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(Received April 18, 1930)

Abstract

A general solution is developed for the motion of electrons in the potential field of the nuclei in a crystal lattice. As usual the energy interaction terms due to nuclear vibration and to the presence of other electrons are neglected; they are to be included later by approximation methods.

It is shown for low energies the wave function becomes a linear combination of the atomic wave functions, the allowed energies approximating the discrete atomic levels; and for high energies the wave function approaches that of the free electron, with the allowed energies a nearly continuous range. However, for electrons coming into the crystal from outside, the crystal becomes impenetrable for those electronic wave-lengths and directions analogous to the beams producing Bragg and Laue beams in x-rays.

The solution is computed for a simple form of potential lattice, and the results are shown to be in quantitative agreement with the experimental results of Davisson and Germer. The phenomenon they call anomalous dispersion is shown to be a natural consequence of the characteristics of the wave function.

Introduction

THE problem of determining the behavior of electrons in crystals has applications in several types of phenomena: in the scattering of electrons from metal surfaces, instanced by the experiments of Davisson and Germer,[1] of G. P. Thomson and others; and in the behavior of metallic conductors.

The first problem in the study of the theory of any of these phenomena is the study of a single electron in a crystal lattice made up of atomic nuclei fixed at their equilibrium centers. The perturbation terms due to nuclear vibration and to the presence of other electrons must then be dealt with by approximation methods.

The simplest possible assumption for the unperturbed electron is that used by Sommerfeld,[2] the wave function being approximately like that of a field-free electron:

$$\psi_\epsilon(W) = N_\epsilon \exp i(W)^{1/2}(ax + by + cz) \tag{1}$$

where W is $8\pi^2\mu/h^2$ times the electronic kinetic energy inside the crystal, and a, b and c are the direction cosines of the electronic motion. This type

[1] This work was begun under the supervision of Dr. Davisson, at the Bell Telephone Laboratories. The writer wishes to express his appreciation of the help the Laboratories in general, and Drs. Davisson and Germer in particular, have given him. He also has obtained many helpful suggestions from Professor E. Wigner.

[2] Sommerfeld, Zeits. f. Physik **47**, 1, (1928).

of wave function is most nearly correct for the most loosely bound electrons, but is not sufficiently correct, even for them, to explain the experiments of Davisson and Germer.

The other type of approximation is to consider the electron behavior as primarily determined by the electric fields of the crystal nuclei. Since the potential wall between the atoms is not infinite, there is a finite probability of an electron belonging originally to one nucleus to change to any other nucleus. This means that in equilibrium the wave function for the electrons in the crystal will be any one of the large number of linear combinations of terms, each term representing the electron in the nth quantum state about the sth nucleus.[3] This is an example of equivalence degeneracy similar to the simple case of the hydrogen molecular ion, and as a result the energy level corresponding to the nth quantum state of a free atom will be split into a large number of very slightly separated levels; in fact, if the crystal is considered infinite in extent, the levels of the free atom will be spread into bands of allowed energies which may or may not be separated from their neighbors by bands of forbidden energies. Of course the wave functions for the electron will be somewhat modified by this proximity of other nuclei, and Bloch[4] has used a wave function which becomes, for an infinitely large crystal:

$$\psi_\epsilon(E) = N_\epsilon \exp i(W)^{1/2}(ax + by + cz) \cdot u(W_a)$$

where E is a function of W and W_a, and u is a linear combination of wave functions representing the electron about the various nuclei with an energy W_a.

This assumption is fairly good for the more tightly bound electrons, in the inner orbits, but for the loosely bound ones, the ones contributing most to the electric conductivity, the field due to the nucleus is so greatly distorted by the neighboring atoms that the undisturbed atomic functions are not particularly good approximations.

At any rate, whatever the potential function happens to be, it can always be represented by the three dimensional Fourier series of the type

$$V = -\frac{h^2}{8\pi^2\mu} \sum_{l,m,n=-\infty}^{\infty} A_{lmn} \exp i(l\alpha x + m\beta y + n\gamma z) \qquad (2)$$

where $\alpha, \beta, \gamma = 2\pi/(d_x, d_y, d_z)$, where the d's are the lengths of sides of the unit lattice cell in the x, y and z directions respectively. The A's are chosen so that V is real and $A_{000} = 0$. This series is applicable to the cubic, tetragonal and orthorhombic systems of lattices, and the generalization to the other systems is obvious. The wave function for such a potential will be obtained, and its properties investigated, in this paper.[5]

[3] Heisenberg, Zeits. f. Physik **49**, 619 (1928). A very good resumé of the subject is given by Slater, Phys. Rev. **35**, 509 (1930).

[4] Bloch, Zeits. f. Physik **52**, 555 (1928).

The Wave Function

A somewhat less general, but considerably simpler form of potential function

$$V = -\frac{h^2}{8\pi^2\mu}\left[\sum_{l=-\infty}^{\infty}\alpha^2 A_{xl}e^{il\alpha x} + \sum_{m=-\infty}^{\infty}\beta^2 A_{ym}e^{im\beta y} + \sum_{n=-\infty}^{\infty}\gamma^2 A_{zn}e^{in\gamma z}\right] \tag{3}$$

will first be considered. The crystal will at first be considered as infinite in extent, and the average potential as zero, so that $A_{x0}=A_{y0}=A_{z0}=0$. If the electronic energy is $h^2W/8\pi^2\mu$ then the Schroedinger equation which must be satisfied can be separated into three equations of the type

$$\Xi'' + \left(W_x\alpha^2 + \alpha^2\sum_l A_{xl}e^{il\alpha x}\right)\Xi = 0 \tag{4}$$

where $W_x\alpha^2+W_y\beta^2+W_z\gamma^2=W$. The complete wave function is $\Psi=\Xi(x)\cdot H(y)\cdot\Omega(z)$, where the equations for H and Ω are similar to Eq. (4).

The independent variables are now changed to $\xi, \eta, \zeta=\alpha x, \beta y, \gamma z$ and then all three equations have the form

$$\Xi'' + (W_x + \sum A_{xl}e^{il\xi})\Xi = 0. \tag{5}$$

The solution of this equation was given by Hill,[6] and is

$$\Xi = N\cdot e^{ik_x\cdot\xi}\cdot\sum_{r=-\infty}^{\infty} b_{xr}(k_x)\cdot e^{ir\xi} \tag{6}$$

where k_x and the b's are to be determined. k_x is given by the equation

$$\sin^2\pi k_x = \sin^2\pi(W_x)^{1/2}\cdot\square(0) \tag{7}$$

where $\square(0)$ is the infinite determinant

$$\begin{vmatrix}
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \dfrac{-A_{x,-1}}{1-W_x} & 1 & \dfrac{-A_{x,1}}{1-W_x} & \dfrac{-A_{x,2}}{1-W_x} & \dfrac{-A_{x,3}}{1-W_x} & \cdots \\
\cdots & \dfrac{-A_{x,-2}}{-W_x} & \dfrac{-A_{x,-1}}{-W_x} & 1 & \dfrac{-A_{x,1}}{-W_x} & \dfrac{-A_{x,2}}{-W_x} & \cdots \\
\cdots & \dfrac{-A_{x,-3}}{1-W_x} & \dfrac{-A_{x,-2}}{1-W_x} & \dfrac{-A_{x,-1}}{1-W_x} & 1 & \dfrac{-A_{x,1}}{1-W_x} & \cdots \\
\cdots & \dfrac{-A_{x,-4}}{4-W_x} & \dfrac{-A_{x,-3}}{4-W_x} & \dfrac{-A_{x,-2}}{4-W_x} & \dfrac{-A_{x,-1}}{4-W_x} & 1 & \cdots \\
\cdots & \dfrac{-A_{x,-5}}{9-W_x} & \dfrac{-A_{x,-4}}{9-W_x} & \dfrac{-A_{x,-3}}{9-W_x} & \dfrac{-A_{x,-2}}{9-W_x} & \dfrac{-A_{x,-1}}{9-W_x} & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots
\end{vmatrix}$$

[5] Equations similar to those considered here were discussed by Bethe, Ann. d. Physik **87,** 55 (1928), but no solution was obtained, Peierls, Ann. d. Physik **4,** 121 (1930) gets an approximate solution, Strutt, Ann. d. Physik **86,** 319 (1928) discussed a one-dimensional case.

[6] Hill, Acta Mathematica **8,** 1 (1886).

This determinant can be expanded into a convergent series of the form

$$\begin{aligned}\square(0) = 1 &- (C_{11}A_{x1}^2 - C_{12}A_{x1}^4 + C_{13}A_{x1}^6 \cdots) \\ &- (C_{21}A_{x2}^2 \cdots) \cdots \\ &+ (C_{121}A_{x1}^2A_{x2} - C_{122}A_{x1}^4A_{x2} + \cdots) \\ &- (C_{131}A_{x1}^3A_{x3} \cdots) + \cdots \\ &+ (C_{1231}A_{x1}A_{x2}A_{x3} \cdots) + \cdots .\end{aligned} \tag{8}$$

The values of some of the C's as functions of W_x are given in Fig. (1).[7] When the series of A's converge at least as rapidly as $A_{xn}=1/2^n$, this expansion

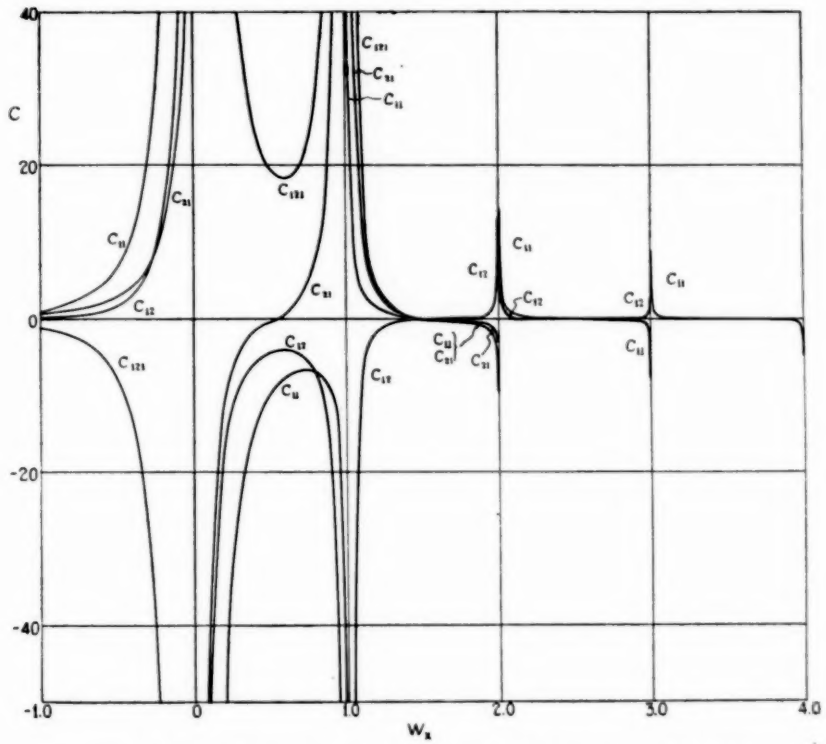

Fig. 1. Values of some of the coefficients in the expansion of $\square$ (0).

is accurate to one part in a thousand if only the terms written above are used.

The b's are obtained by solving the equations

$$[(k_x + r)^2 - W_x]b_{x,r} - \sum_{l=-\infty}^{\infty} A_{xl}b_{x,r-l} = 0 \tag{9}$$

where r can have any integral value from plus to minus infinity.

[7] The writer is very much indebted to Mr. B. L. Snavely for computing the values of a number of the functions discussed in this paper.

A generalization of Hill's arguments shows that a solution of the Schroedinger equation using the general potential function given in Eq. (2) will be of the form

$$\psi = N \exp i(\kappa_x x + \kappa_y y + \kappa_z z) \sum_{r,s,t=-\infty}^{\infty} B_{rst} \exp i(r\alpha x + s\beta y + t\gamma z) \qquad (10)$$

where the relations between the κ's are given by the equation

$$S(\kappa_x, \kappa_y, \kappa_z; \alpha, \beta, \gamma) = S(aW^{1/2}, bW^{1/2}, cW^{1/2}; \alpha, \beta, \gamma) \cdot \square(0,0,0,) \qquad (11)$$

where $\square(0, 0, 0,)$ is a determinant similar to $\square(0)$. The function

$$S(x, y, z; \alpha, \beta, \gamma) = (x^2+y^2+z^2) \prod_{l,m,n=-\infty}^{\infty}{}' \left[1 - \frac{2l\alpha x + 2m\beta y + 2n\gamma z - x^2 - y^2 - z^2}{l^2\alpha^2 + m^2\beta^2 + n^2\gamma^2}\right]$$

where the infinite product does not include the term for which $l=m=n=0$, and a, b and c are the direction cosines which the electronic motion would have if all the A's were zero. For a two-dimensional case $S(x, y; \alpha, \beta)$ is the product of the elliptic functions $H(x+iy) \cdot H(x-iy)$, where the periods of these functions are $K=\alpha/2$ and $K'=\beta/2$. For the one-dimensional case discussed by Hill, $S(x; \alpha)$ is $\sin^2(\pi x/\alpha)$ as given in Eq. (7). The B's are given by the equations

$$[(\kappa_x + r\alpha)^2 + (\kappa_y + s\beta)^2 + (\kappa_z + t\gamma)^2 - W]B_{r,s,t} + \sum_{l,m,n} A_{lmn} B_{r-l,s-m,t-n} = 0.$$

Expression (10) is of natural form; that of a free electron whose direction cosines of motion are proportional to κ_x, κ_y and κ_z, multiplied by a function representing the distortion of the wave function due to the periodic variation of the potential function. For low energies this distorting function will be a Fourier expansion of one of the linear combinations of atomic wave functions discussed earlier. In this case Eq. (9) is the form used by Bloch.

One property of (9) must be emphasized, however. The coefficients κ_x, κ_y, κ_z, in the "field-free-electron" factor are not equal to $W^{1/2}(a, b, c)$ as they would be if the A's all equalled zero, as for Eq. (1). For values of $a(W)^{1/2}$ near $l\alpha/2$, or $b(W)^{1/2}$ near $m\beta/2$, or $c(W)^{1/2}$ near $n\gamma/2$ (i.e., near the singular points of the determinant or near the maximum points of the function S) the κ's differ considerably from the values $(W)^{1/2}(a, b, c)$, and for certain ranges become complex.

In crystals of infinite extent, the values of W and a, b and c for which any of the κ's become complex are not allowed; for in these cases the wave function contains a real exponential factor which becomes infinite at plus or minus infinity. Even in the case of finite crystals, it is seen that the amplitude of wave functions for which a κ becomes complex is negligible in the interior of the crystal. Thus for crystals of size greater than, say, a thousand atoms along a side, electrons with energies for which a κ is complex are not present inside the crystal.

This means that the periodic variation of potential inside the crystal creates bands of forbidden energies inside the crystal, even for electronic energies greater than the maximum potential energy, a somewhat surprising result. However, this only means that when electrons outside a crystal have energies such that their wave-number components are integral multiples of the reciprocal lattice spacing, they are reflected strongly back at the surface of the crystal. That this is true experimentally has been shown by Davisson and Germer.

These bands of forbidden energies are very wide for low energies, but become very narrow for higher energies. In other words, the allowed bands of energy are very narrow for low energies, corresponding quite closely to the atomic levels; but for energies larger than the maximum potential energy nearly every energy is allowed. Thus the general solution shows a gradual transition from purely atomic states to states of the free electron, as general considerations have shown it should.

A Simple Example

It will be of interest to examine in detail the solution for a very simple form of potential variation. The form

$$V = -\frac{h^2}{8\pi^2\mu}[2\alpha^2 A_x \cos \alpha x + 2\beta^2 A_y \cos \beta y + 2\gamma^2 A_z \cos \gamma z] \tag{12}$$

is not a particularly good approximation to the lattice field, but its solution is not too difficult, and the quantitative check of the computed results with experiment leads one to believe that it is not too bad an approximation when dealing with electrons of high energy. It is, of course, a very poor approximation for the low energy, "bound" electrons, and care should be used in applying its results.

The three Schroedinger equations which must be solved are Matthieu equations

$$\Xi'' + (W_x + Ae^{i\xi} + Ae^{-i\xi})\Xi = 0. \tag{13}$$

The solution is the generalized Matthieu function,[8] of the form given in Eq. (6), where the values of k_x are given by Eq. (7) when $A_{x1} = A_{x-1} = A$, and $A_{xn} = A_{x-n} = 0$, for n greater than unity, in the determinant $\square(0)$.

The values of k_x^2 as a function of A and W_x are shown by means of the contour map in Fig. 2. The shaded areas are the values of A and W_x where k_x is complex. It is to be noticed that these areas are larger the larger A is, and are smaller the larger W_x is. The area included between the diagonal dotted lines radiating from $A = W_x = 0$ represents the values of W_x less than the maximum and greater than the minimum potential energy. The values of the contours for k_x^2 are equal to the values of W_x when $A = 0$, as would be expected. The narrowing of the unshaded bands of energy as A increases

[8] E. C. G. Poole, Proc. Lond. Math. Soc. **20**, 374 (1921); B. van der Pol and M. J. O. Strutt, Phil. Mag. **5**, 18 (1928).

illustrates the transition from the continuous allowed levels when $A=0$ to the discrete levels when A is infinite.

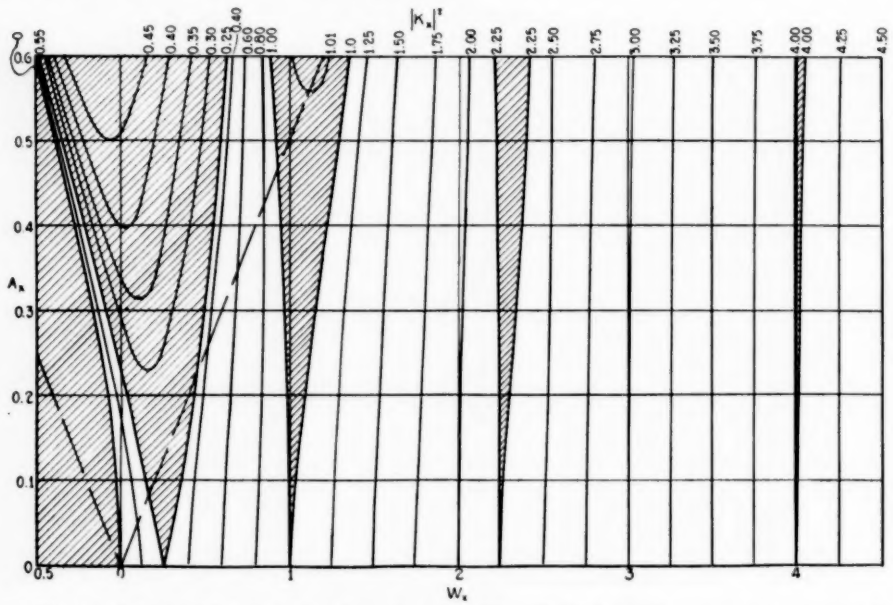

Fig. 2. Values of k_x^2 as a function of A and W_x. Shaded portions represent areas where k_x is complex and equals $(n/2)+ig(W_x)$, where g is real.

The difference between the character of the levels for one atom and for an infinite lattice is shown in Fig. 3. Curve (*a*) gives the potential energy cross section for a single "atom" with its discrete set of allowed levels, and

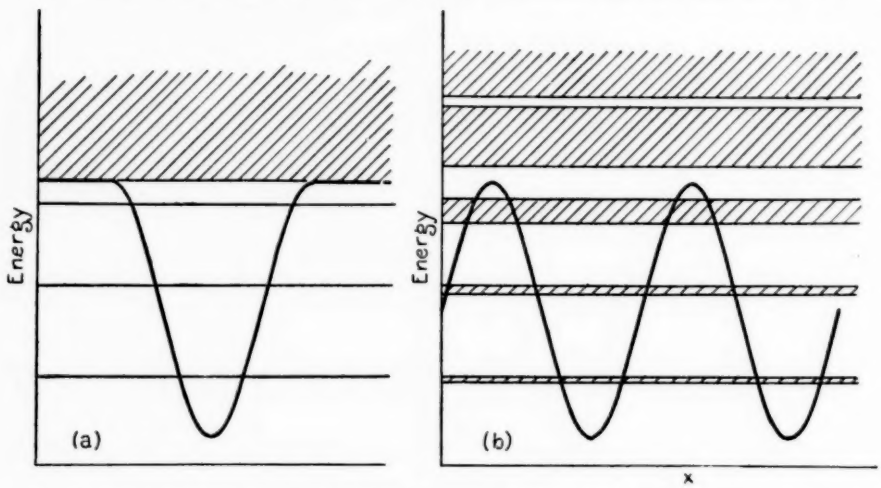

Fig. 3. Potential function and allowed energies for a single "atom" and for a crystal of infinite extent. Horizontal lines represent discrete levels, and shaded areas represent continuous allowed bands.

curve (*b*) gives the potential function for an infinite lattice with its bands of allowed levels.

The difference between W_x and the real values of k_x for a given value of A can be given by considering W_x as a function of k_x and defining

$$f_x(k_x) = W_x(k_x) - k_x^2. \tag{15}$$

Values of f_x for real values of k_x are given in Fig. 4 for a particular value of A.

The value of A will be chosen to be 1/4 for the calculations below, since for this value, and for a lattice spacing of 3·5 Angstrom units, the difference between the maximum and minimum potential energy in the crystal will be about 36 electron volts, a reasonable variation.

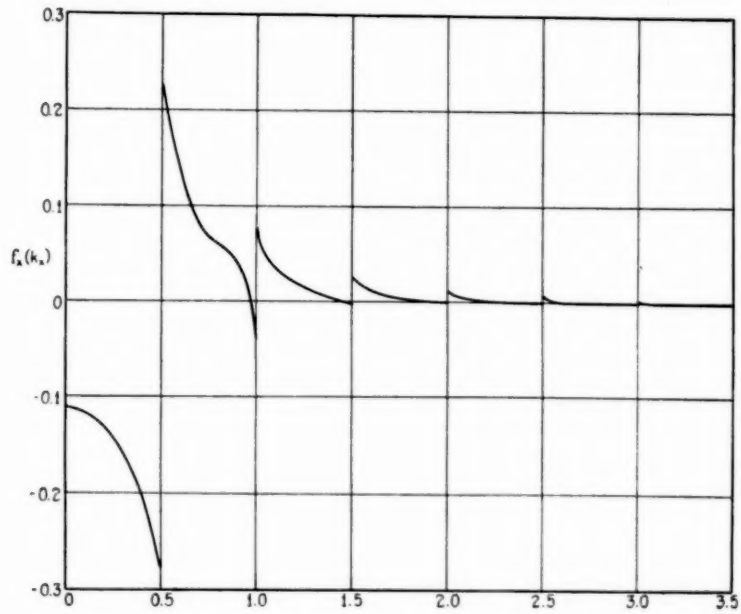

Fig. 4. Values of $f(k_x)$ for real values of k_x, for $A = 1/4$.

The Fourier coefficients, $b_{xn}(k_x)$, can next be computed by means of Eq. (9), which in this special case can be transformed[9] into one or the other of the following continued fractions

$$\frac{b_{x,r}}{b_{x,r+1}} = \cfrac{A}{S_r - \cfrac{A^2}{S_{r-1} - \cfrac{A^2}{S_{r-2} - \cdots}}}$$

$$\frac{b_{x,r}}{b_{x,r-1}} = \cfrac{A}{S_r - \cfrac{A^2}{S_{r+1} - \cfrac{A^2}{S_{r+2} - \cdots}}} \tag{16}$$

[9] E. C. G. Poole, Proc. Lond. Math. Soc. **20**, 382 (1921).

where $S_r=(k_x+r)^2-W_x$. Values of b_{xr} are computed in terms of b_{x0} and the value of b_{x0} adjusted so that $\sum_r b_{xr}^2=1$, for normalization purposes. Values of the b's for $A=1/4$ for various real values of k_x are shown in Fig. 5.

It can be shown in general, by symmetry arguments, that when $k_x=n/2$ (n an integer) $b_{x,r}=\pm b_{x,-n-r}$. In intermediate cases, as is seen in the curves, b_{x0} is very much larger numerically than any of the other b's.

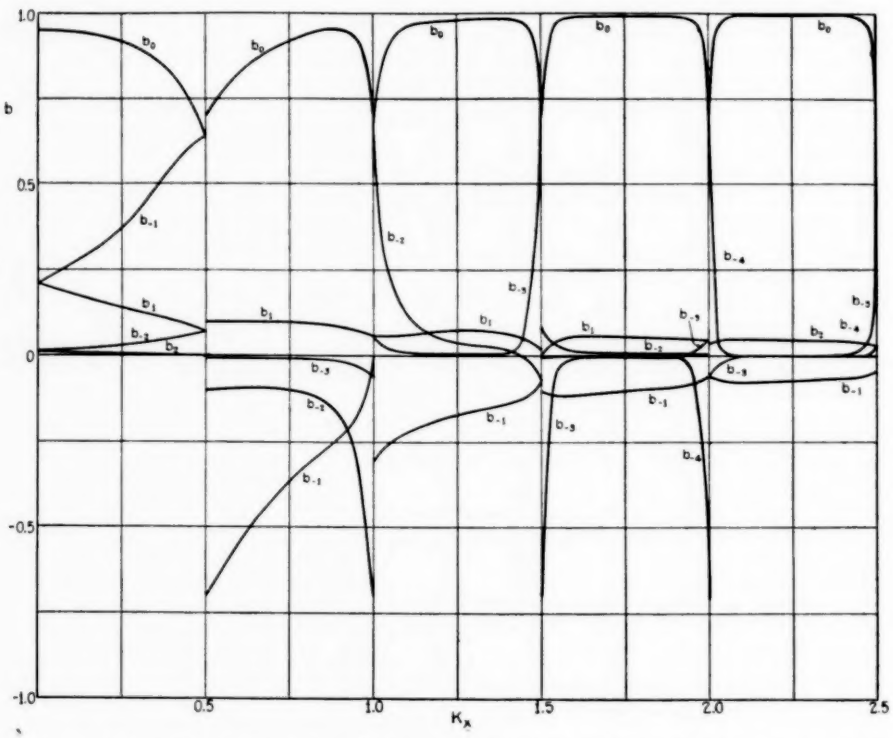

Fig. 5. Values of the Fourier coefficients $b_i(k_x)$ for real values of k_x, for $A=1/4$. Coefficients not shown in this figure are negligibly small.

Scattering from Crystal Surfaces

Thus for this simple case it is possible to obtain an exact solution for the motion of electrons inside a potential lattice. Let us see how nearly these results check with experiments with electrons of high energies.

Such experiments have been chiefly concerned with the scattering of electrons from the surface of a crystal. A simple model of this experiment would be a plane electron wave of kinetic energy $h^2E/8\pi^2\mu$ outside the crystal. If the potential outside is zero, that inside will be $h^2V_0/8\pi^2\mu$ plus the V given in Eq. (12), since the average potential inside the crystal is less than that outside. The values of the W's used will then be such that $W_x\alpha^2+W_y\beta^2+W_z\gamma^2=W=E+V_0$.

The wave function inside the crystal (positive values of x) will be given by the product of three factors similar to Eq. (6). Then, since the wave

function must be continuous in value and normal gradient at the crystal surface, the wave function outside must be

$$\Psi_0 = \sum_{m,n=-\infty}^{\infty} C_{mn} \exp i\{[E-(k_y+m)^2\beta^2-(k_z+n)^2\gamma^2]^{1/2}\cdot x + (k_y+m)\beta y + (k_z+n)\gamma z\} + \sum_{m,n=-\infty}^{\infty} D_{mn} \exp i\{-[E-(k_y+m)^2\beta^2-(k_z+n)^2\gamma^2]^{1/2}\cdot x + (k_y+m)\beta y + (k_z+n)\gamma z\} \tag{18}$$

where the C terms represent beams impinging on the surface and the D terms represent beams coming from the surface. But to fit the case we were considering, where there was only one incident beam with the direction cosines a, b and c, we must make all the C's equal to zero except, say, C_{00}, and then make $b^2E=k_y^2\beta^2$ and $c^2E=k_z^2\gamma^2$. To do this we must introduce other internal beams, due to the secondary internal reflections from the surface.

Then the complete wave function inside the crystal is

$$\Psi_i = \sum_{r,s=-\infty}^{\infty} F_{rs} \exp i[k_x(rs)\alpha x + (k_y+r)\beta y + (k_z+s)\gamma z] \cdot \sum_{l,m,n} B_{lmn}(rs)\cdot \exp i(l\alpha x + m\beta y + n\gamma z) \tag{19}$$

where $B_{lmn}(rs)=b_{xl}(k_x(rs))\cdot b_{ym}(k_y+r)\cdot b_{zn}(k_z+s)$, and where F_{00}, the coefficient of the primary internal beam, can be taken as unity. The value of $k_x(rs)$ is determined by the value of $W_x(rs)$, where

$$\alpha^2 W_x(rs) = E + V_0 - (k_y+r)^2\beta^2 - (k_y+s)^2\gamma^2 - \beta^2 f_y(k_y+r) - \gamma^2 f_z(k_z+s).$$

No negative value of k_x is included, since the other boundary of the crystal is considered as being at x equals positive infinity, and no beams reflected from its surface are present.

The intensity of these secondary internal rays is determined by $|F_{rs}|^2$ and will be shown to be small compared to $|F_{00}|^2$. Since also the B's decrease rapidly (except for special cases considered later) for increasing l, m, n, to a good approximation we can neglect all except the $B_{l00}(rs)$ for every beam except the primary one, where $r=s=0$.

Then the boundary conditions determining the relative magnitudes of the D's and F's for all C's equal to zero except C_{00} are, approximately

$$\begin{aligned} C + D_{00} &= \sum_l B_{l00}(00) \\ C - D_{00} &= \frac{\sum_l (k_x+1)\alpha B_{l00}(00)}{(E-k_y^2\beta^2-k_z^2\gamma^2)^{1/2}} \end{aligned} \tag{20}$$

for the incident and primary reflected and refracted beams. Here $C=C_{00}$ and $k_x=k_x(00)$ for brevity. Also

$$D_{rs} = \sum_l [B_{lrs}(00) + F_{rs} B_{l00}(rs)]$$

$$-D_{rs} = \frac{\sum_l [(k_x + l) B_{lrs}(00) + F_{rs}(k_x(rs) + l) B_{l00}(rs)] \alpha}{(E - (k_y + r)^2\beta^2 - (k_z + s)^2\gamma^2)^{1/2}} \tag{21}$$

for the secondary beams outside and inside, since all the other C's are zero.

These equations will hold to a good approximation except in the special cases when F_{rs} becomes of the same order of magnitude as F_{00} (this can only happen when $B_{lrs}(00)$ is of the same order as $B_{000}(00)$, and then not necessarily). In this case the D's other than D_{rs} will be small anyhow, and the resulting inaccuracy in the determination of the reflected intensities will be small even in this special case.

Then the ratio between the incident current of electrons and the regularly reflected current is

$$\left|\frac{D_{00}}{C}\right|^2 = \left|\frac{\sum_r [(a(E)^{1/2}/\alpha) - k_x - r] b_{xr}(k_x)}{\sum_s [(a(E)^{1/2}/\alpha) + k_x + s] b_{xs}(k_x)}\right|^2 \tag{22}$$

When k_x is not near half integral values, it is nearly equal to $(a^2E + V_0)^{1/2}/\alpha$, and b_{x0} is the only not-negligible b_x. Then the formula reduces to

$$\left|\frac{D_{00}}{C}\right|^2 = \left[\frac{a(E)^{1/2} - (a^2E + V_0)^{1/2}}{a(E)^{1/2} + (a^2E + V_0)^{1/2}}\right]^2$$

which is the intensity of reflection when $A = 0$. That is, except for special values of k_x, the crystal behaves as though it were a hollow of uniform potential $-h^2V_0/8\pi^2\mu$ with no periodic potential variation at all.

When $k_x = n/2$, however, we have seen that $b_{x,s} = \pm b_{x,-s-n}$, and substituting $-(s+n)$ for r in Eq. (22) it is seen that

$$\left|\frac{D_{00}}{C}\right|^2 = \left[\frac{\pm\sum_s [(aE^{1/2}/\alpha) + (n/2) + s] b_{xs}}{\sum_s [(aE^{1/2}/\alpha) + (n/2) + s] b_{xs}}\right]^2 = 1.$$

For the complex values of k_x, $|D_{00}/C^2| = 1$, but there is a change of phase on reflection. That is, the crystal is perfectly reflecting for every value of electronic energy and direction of incidence which has a value of W_x for which k_x is a half integer or is complex. These values of W_x for any value of A are represented by the shaded areas in Fig. 2.

Of course in an actual crystal the reflected intensity for these values of W_x will be considerably less than unity, because a number of electrons will interact with the crystal atoms as they traverse the lattice. In any case, however, the maximum reflection intensity will be for values of W_x somewhere within the shaded areas in Fig. 2, and can be represented by the equation

$$W_{xn} = (n^2/4) + G_n(A) \tag{23}$$

where G is a small quantity compared to $1/4$, except for the case $n=1$.

When the incident electron stream is normal to the crystal surface, $W_y = f_y(0)$ and $W_z = f_z(0)$, since k_y and k_z must both equal zero. Equation (18) reduces to

$$W_x\alpha^2 = E + V_p$$

where $V_p = V_0 - \beta^2 f_y(0) - \gamma^2 f_z(0)$, which is larger than V_0 since the $f(0)$'s are negative quantities.

In this case the relative intensity of the reflected beam will be a maximum when

$$E_n = (n^2\alpha^2/4) + \alpha^2 G_n(A) - V_p \tag{24}$$

from Eq. (23). The ideal curve for a typical case is given in Fig. 6. In the actual case, as was previously pointed out, the maxima are less than unity and probably decrease in height for increasing n, since the peaks are narrower and the chance of losing energy is greater. The experimental curves of Davisson and Germer[10] for nearly normal incidence show just such characteristics.

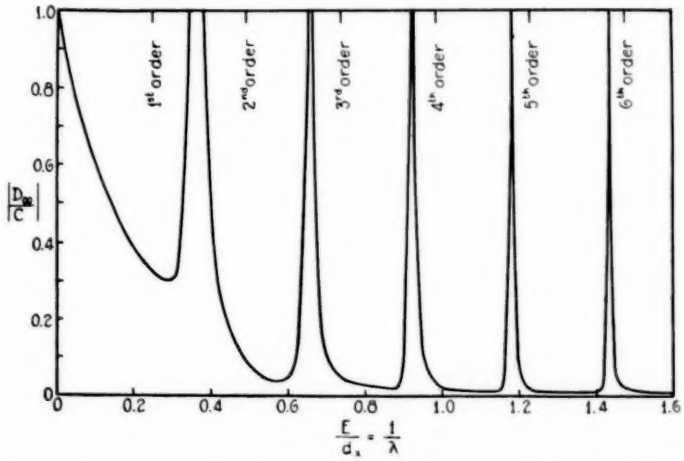

Fig. 6. Relative intensity of the regularly reflected beam as a function of the electronic wave number. The incident beam is normal to the 111 surface of a nickel crystal. Lines marked 1st order, etc., indicate positions of strong x-ray reflection for the same crystal.

There will also be the other scattered beams represented by the coefficients D_{mn} in Eq. (19) whose direction cosines will be $(E - m^2\beta^2 - n^2\gamma^2)^{1/2}/E^{1/2}$, $m\beta/E^{1/2}$ and $n\gamma/E^{1/2}$, whose relative intensities will vary with E, but will in general be much smaller than unity.

For an obliquely incident beam whose plane of incidence is parallel to the z axis we have

$$W_x\alpha^2 = E\cos^2\theta + V_a - \beta^2 f_y\left(\frac{E^{1/2}\cdot\sin\theta}{\beta}\right)$$

[10] Davisson and Germer, Proc. Nat. Acad. Sci. **14**, 622 (1928).

where $V_a = V_0 - \gamma^2 f_z(0)$ is larger than V_0 but smaller than V_p, and where θ is the angle of incidence.

The values of θ and E for a regularly reflected beam of maximum intensity will be such that

$$W_{xn}\alpha^2 = (n^2\alpha^2/4) + \alpha^2 G_n(A)$$

similarly to Eq. (23). Substitution in the equation for $W_x\alpha^2$ gives

$$E_n \cos^2\theta_n = (n^2\alpha^2/4) - V_n + \beta^2 f_y\left(\frac{(E_n)^{1/2}\sin\theta_n}{\beta}\right) \tag{25}$$

where $V_n = V_a - \alpha^2 G_n$, and where E_n and θ_n signify the values of E and θ for maximum regular reflection. Since the quantity f_y is small for most values of its argument (see Fig. 4) we see that the wave-length $1/E_n^{1/2}$ plotted against $\cos\theta_n$ gives in general a straight line going through the origin. However since f_y is large and discontinuous for values of E_n and θ_n near where

$$E_n^{1/2}\sin\theta_n = m\beta/2 \tag{26}$$

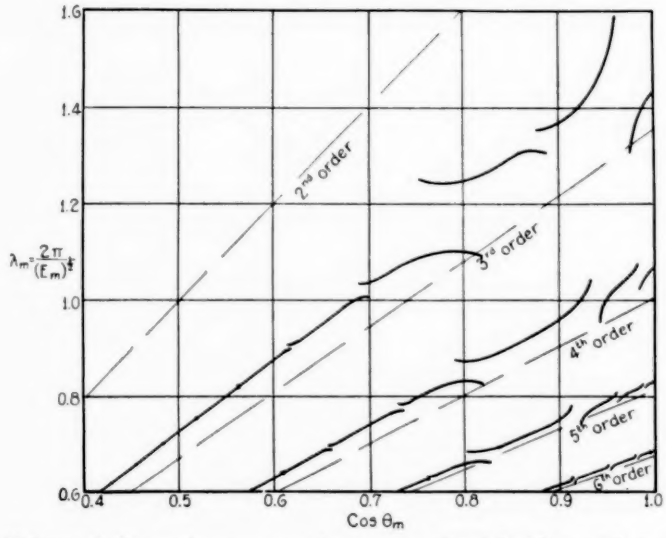

Fig. 7. Values of electronic wave number and angle of incidence of electron beam for strong regularly reflected beam. The crystal is nickel, the surface the 111 plane. Broken lines indicate positions of analogous x-ray reflection.

the curve deviates from a straight line near these values, and is discontinuous. A curve of $1/E_n^{1/2}$ against $\cos\theta_n$ for values of α, β and A corresponding to a nickel crystal is shown in Fig. 7.[11]

[11] The analysis here has been for the case when the crystal surface is the 100 plane, perpendicular to a crystal axis. In the experiments of Davisson and Germer, the crystal surface was the 111 plane, oblique to the crystal axes. In this case, both f_x and f_y vary, and although the discontinuities are of the same character as that given above, their shape is more complicated. Eqs. (25) and (26) still hold, however, if α and β are now considered as the distance between atom planes parallel and perpendicular to the surface, respectively, and $\Phi(E_n^{\frac{1}{2}}\sin\theta_n/\beta)$, a function of f_x and f_y, be substituted for f_y in Eq. (25). Fig. 7 has been computed by means of these revised equations.

When the experimental curves[12] for this case are studied it is seen that not only is the general form of the curves similar, discontinuities and all, but that the positions of the discontinuities correspond. The shape of the curves near the discontinuities does not fit exactly, but if a better approximation to the actual potential function were used in the calculations, the correspondence would probably be better.

The physical explanation of these discontinuities is that for $E_n \sin^2 \theta_n = m^2\beta^2/4$ there is resonance, and therefore strong damping, in the y direction, and nearly all the electrons are reflected back in a direction exactly opposite to the incident beam, leaving none to be regularly reflected. This phenomenon was given the tentative name of "anomalous dispersion" by Davisson and Germer, and in a way this term is correct, for it is due to a simultaneous resonance of the x and y components of the electronic wave number, and a consequent damping out of the wave function in the interior of the crystal.

The other scattered beams in the x, y plane come off at angles ϕ_m, where

$$\sin \phi_m = \sin \theta + m\beta/E^{1/2}. \tag{27}$$

It can be seen from Eq. (21) that their relative intensities will be

$$\left|\frac{D_{m0}}{C}\right| = \left|\frac{b_{ym}(E^{1/2}\sin\theta)}{b_{y0}(E^{1/2}\sin\theta)} \times \frac{\sum_{rs}(k_x' + s - k_x - r)\, b_{xr}(k_x)\cdot b(k_x')}{\sum_{ln}\left(k_x' + l + \frac{E^{1/2}\cos\Phi}{\alpha}\right)\left(k_x + n + \frac{E^{1/2}\cos\theta}{\alpha}\right) b_{xn}(k_x) b_{xl}(k_x')}\right|^2 \frac{E\cos^2\theta}{\alpha^2}$$

where k_x' is the $k_x(mo)$ of the beam reflected back into the crystal at the surface, and is a function of the energy W_x', where

$$\alpha^2 W_x' = E + V_a - (E^{1/2}\sin\theta + m\beta)^2 - \beta^2 f_y\left(\frac{E^{1/2}\sin\theta}{\beta} + m\right)$$

These secondary internal beams will make a slight change in the magnitude of the primary internal beam, but this can be neglected. The quantity b_{ym} is only large when $E^{1/2}\sin\theta$ is near the value $-m/2$, corresponding to reinforcement due to the y, z planes of atoms, and, when E and θ also satisfy Eq. (23), corresponding to the case of "anomalous dispersion" of the regularly reflected beam. The quantity $|D_{m0}/C|^2$ also shows other maxima analogous to the various Laue beams in x-ray scattering.

Conclusion

Thus it has been seen that for high energy electrons even the simple potential function used above gives results in good accordance with experiment. This accordance becomes less and less good as we consider electrons with less and less energy, and the results probably do not fit at all for the

[12] Davisson and Germer, Proc. Nat. Acad. Sci. **14**, 624 (1928). Later (unpublished) curves show a more complete agreement.

tightly bound electrons in the inner atomic shells, where the allowed energies are narrow bands very slightly different from the simple discrete atomic levels. For these electrons, also, the interaction between electrons cannot be neglected.

However for those electrons whose energy is greater than $-h^2V_0/8\pi^2\mu$ it seems likely that the results of the simple case discussed above will be indicative. So that while this simple case will not tell us anything about ferromagnetism, for instance, or of any other crystal property which depends on the inner bound electrons, it may be of help in discussing those properties which depend primarily on the high energy free electrons, such as electric conductivity. We have seen that for the still higher energy electrons used in scattering experiments, the agreement with experiment is very good.

When the stationary states inside a crystal of finite size (say a rectangular one whose edges are Ld_x, Md_y, Nd_z respectively, where L, M and N are integers) are considered, it is seen that the wave functions are

$$\psi_{rst} = \frac{(2)^{1/2}}{(L^2d_x^2 + M^2d_y^2 + N^2d_z^2)^{1/2}} \sum_{l,m,n} B_{lmn}(r,s,t) \sin\left[\left(\frac{r}{2L} + l\right)\alpha x + \left(\frac{s}{2M} + m\right)\beta y + \left(\frac{t}{2N} + n\right)\gamma z\right]$$

where the fractions $r\alpha/2L$, $s\beta/2M$ and $t\gamma/2N$ (r, s, t integers) replace the variables κ_x, κ_y and κ_z, and where the B's are normalized so that $\sum_{l,m,n} B_{lmn}^2 = 1$. From this it can be seen that the distribution of electrons in terms of $r^2\alpha^2/L^2$, $s^2\beta^2/M^2$, $t^2\gamma^2/M^2$ is a normal Fermi one. But, since the energy is a complicated function of these quantities, the electron distribution in energy is different from that of the completely free electron.

AN EXTENSION OF HOUSTON'S AND SLATER'S MULTIPLET RELATIONS

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Abstract

Expressions giving the change in the positions of the energy levels with change in electron coupling are derived. The change in g-values is discussed also. The method of derivation is a short-cut of the rigorous detailed method and therefore simpler. One knows the form of the equations of which the desired energies must be roots. The coefficients of these equations are determined by the known results for extreme couplings. This method does not always give all coefficients, but even in complicated cases useful relations between the energy levels are found.

FOR the case of two electrons one of which is in an s-state, Houston[1] obtained expressions for the four resulting levels for any coupling strength. Houston considered the coupling and the spin-orbit interaction as perturbations and calculates by quantum mechanics the first order perturbations to the energy. He also derived expressions for the g-values and for the intensities to show their variation with change of coupling.

As soon as one removes the restriction that one of the two electrons is in an s-state the method used by Houston becomes very complicated. Dr. Laporte has informed me that one can apply Houston's results to configurations like p^5s and d^9s by considering the p^5 and the d^9 group as if it were a single p, or d electron and by taking, in addition, the spin orbit interaction with a negative sign. This remark led to the considerations outlined in this paper.

It is possible to get the main results and often even the complete results of the detailed theory as used by Houston by a simplified procedure. One knows from perturbation theory exactly what type of equations will be obtained for the first order perturbations to the energy. Furthermore one knows from simple considerations of the vector model the energies in extreme (j, j) coupling and in the extreme Russell-Saunders coupling.[2] In the latter case the results of the vector model have to be supplemented with the results derived by Slater[3] which give relations among the distances of various multiplets of a configuration. Our knowledge of these extreme cases is sufficient to fix the most important coefficients, sometimes all coefficients, in the general equation for the energy perturbation.

[1] W. V. Houston, Phys. Rev. **33,** 297 (1929).

[2] Extreme (j,j) coupling means no interaction between the electrons, extreme Russell-Saunders coupling large interaction, much larger than the interaction between spin and orbit.

[3] J. C. Slater, Phys. Rev. **34,** 1293, (1929).

From the formulas obtained in this way one hopes to be able to predict the position of unknown levels but in this respect the results are rather disappointing. First of all one must not forget that we consider only the first order perturbation; thus neither the coupling nor the spin-orbit interaction may be too large. This excludes the very light and the very heavy elements. In the former the singlet-triplet and similar distances are often of the same order as the total energy, in the latter this is the case for multiplet separations. But much worse for their use as predictors of levels is the special form which most of the resulting expressions have. Consider for instance a triplet and a connected singlet level. If one knows the singlet and two levels of the triplet one can predict with great accuracy the position of the third triplet level. This great accuracy, however, is due to the fact that this triplet level is not displaced very much in going from one extreme coupling to the other. A mere guess would have given a fair result. In practice, on the contrary, one always knows the triplet and wants to know the position of the singlet. Its variation in position with change of coupling is very large and a small error in the known triplet causes a large error in the predicted position of the singlet. Of course the percentage error one makes in predicting the triplet level is the same as for the singlet level, but for the latter this corresponds to a much larger absolute error in position. In general the predictions will be most accurate if the singlet is not very far away from the triplet. It is to be regretted that in practice one just always needs the cases where the prediction is most unusable! What is said here for the simple example of a singlet and a triplet holds also for more complicated cases.

Before demonstrating the method by examples we will describe the general equation for the energy perturbation mentioned above. Let us denote the perturbation energies by $X_1, X_2, \ldots$. For instance in the case of two electrons X_1 is the coupling energy, X_2 and X_3 are the spin orbit interactions[4] for both electrons, X_4 might be the energy in an external magnetic field in case we want the g-values, etc. If, in the configuration which we consider, a certain value of the total moment J occurs for n levels, their energy perturbations E will be the roots of an equation of the nth degree, homogeneous in E and all the X's.

$$E^n + E^{n-1}\Sigma a_k X_k + E^{n-2}\Sigma b_{kl} X_k X_l + E^{n-3}\Sigma c_{klm} X_k X_l X_m + \cdots = 0. \quad (1)$$

It is obvious that only in a few cases our knowledge of the extreme couplings is sufficient to determine *all* the unknown coefficients. But we can be glad that such rather simple cases form quite an interesting group for which there is a large amount of known material and which is also of some interest with regard to the prediction of levels.

In more complicated cases not all coefficients can be found. For example, the coefficients of products of different X's are often not obtainable by our method. But even if we know only the first coefficient, that of E^{n-1}, it gives

[4] We neglect the interaction between the one spin and the other orbit. See W. Heisenberg. Zeits. f. Physik **39**, 499 (1926).

us interesting information. This coefficient is the sum of the roots, with the negative sign, and is, as we see from (1), a linear function of the perturbation energies. From this one can derive relations among the energies similar to the constancy of g-, Γ-, and intensity sum rules.

Demonstration of the Method by Examples

The configuration p^4. As we are dealing with equivalent electrons we have only one coupling parameter X and one parameter to measure the spin orbit interaction, which will be denoted by A. This configuration gives rise to one level with $J=1$, two with $J=2$ and also two with $J=0$. In the extreme

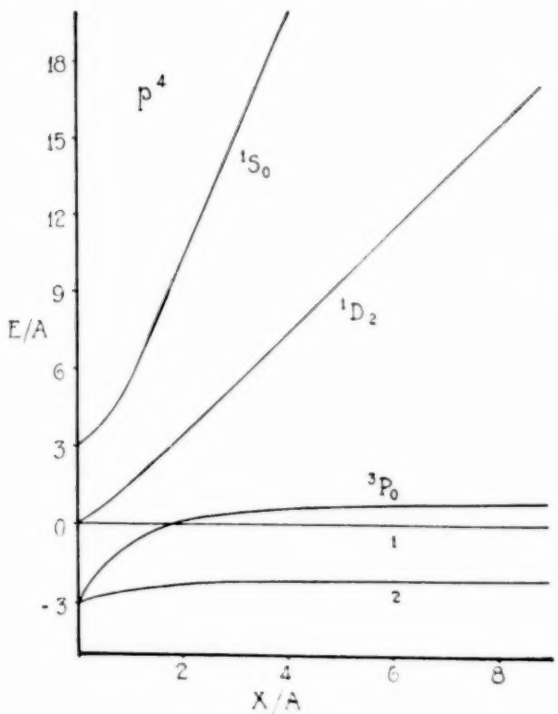

Fig. 1. Change in coupling for configuration p^4.

Russell-Saunders coupling they would be arranged in an inverted ^3P, a ^1D and a ^1S. The total separation of the triplet is equal to the doublet separation which one of the p electrons would show if it alone were present.[5] We will measure the energies in wave number units and for convenience put the ideal triplet separation equal to $3A$. The arrangement in the extreme (j, j) coupling can be found as follows.[6] The lowest state will have as many electrons as are allowed by the Pauli principle with their individual $j=\frac{1}{2}$. Thus in this state there are two electrons with $j=\frac{1}{2}$ and the remaining two have $j=1\frac{1}{2}$,

[5] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

[6] L. Pauling and S. Goudsmit, The Structure of Line Spectra, McGraw-Hill 1930, page 256.

giving rise to one level with $J=2$ and another with $J=0$. Next higher will be the state with one electron with $j=\frac{1}{2}$ and three with $j=1\frac{1}{2}$, producing two levels with $J=0$ and 1. The distance between these levels and the former group will be just the doublet separation of one of the p electrons, as just one changed its j from $\frac{1}{2}$ to 1 and this is again the distance which we call $3A$. Finally again $3A$ higher lies one level with $J=0$ which results from all four electrons having $j=1\frac{1}{2}$. In Figure 1 the left side represents the extreme (j, j) coupling, the right side tends to the extreme Russell-Saunders coupling. As reference level we will take the single level with $J=1$ and give the other levels by their distance E from this level.[7] Our equations (1) are thus for this example:

$$\begin{aligned} J &= 1: E_1 = 0 \\ J &= 0: E_0^2 + E_0(aX + bA) + cX^2 + dXA + eA^2 = 0 \\ J &= 2: E_2^2 + E_2(pX + qA) + rX^2 + sXA + tA^2 = 0. \end{aligned} \tag{2}$$

Now for $X=0$, in the extreme (j, j) coupling the results must be

$$X = 0: E_0 = -3A \text{ and } +3A;\ E_2 = 0 \text{ and } -3A.$$

From this follows immediately for the coefficients:

$$b = 0,\ e = -9;\ q = 3,\ t = 0.$$

In the extreme Russell-Saunders coupling we consider first the finite roots.

$$X \text{ large}: \quad E_0 = +A;\ E_2 = -2A.$$

This gives

$$c = 0,\ d = -a;\ r = 0\ \ s = 2p.$$

The large roots in that case will be

$$E_0 = -aX;\ E_2 = -pX.$$

They represent the $^1S_0$ and the $^1D_2$. Now we need the result obtained by Slater in his above quoted paper, informing us that in the extreme Russell-Saunders coupling the order of the levels is as in our Fig. 1 and that the distance between ^3P and ^1S is 5/2 times that between ^3P and ^1D. If we thus put $-p=2$, we must take $-a=5$ in order to agree with those results. The total set of expressions for p^4 thus becomes

$$\begin{aligned} J &= 1: E_1 = 0 \\ J &= 0: E_0^2 - 5XE_0 + 5XA - 9A^2 = 0 \\ J &= 2: E_2^2 - (2X - 3A)E_2 - 4XA = 0. \end{aligned} \tag{3}$$

For practical purposes it is easiest to choose A as the unit of energy as is done in Fig. 1. The figure shows the interesting crossing over of the triplet

[7] In some cases the formulas become somewhat simpler if one chooses the center of gravity of a multiplet or of all the levels as reference level, but in practice it is easier to do it the way it is done here.

levels with $J=0$ and $J=1$. This explains for instance the partial inversion of this triplet as observed in tellurium.[8] With this same example we can check our expressions. The sum of observed E's for the levels with $J=0$ is $5X=-44+18441=18397$. For the levels with $J=2$ this sum is equal to $2X-3A$ and is observed to be $-4751+5808=1157$. It follows

$$X = 3680 \quad A = 2068, \quad X/A=1.78.$$

The energies calculated with these values are:[9]

$J=0$	calc.	-13	obs.	-44
		$+18410$		$+18441$
$J=2$		-4970		-4751
		$+6127$		$+5808.$

Figure 2 represents the interval ratio of the triplet as a function of X/A. This figure may be usful to predict roughly the singlets if one knows the trip-

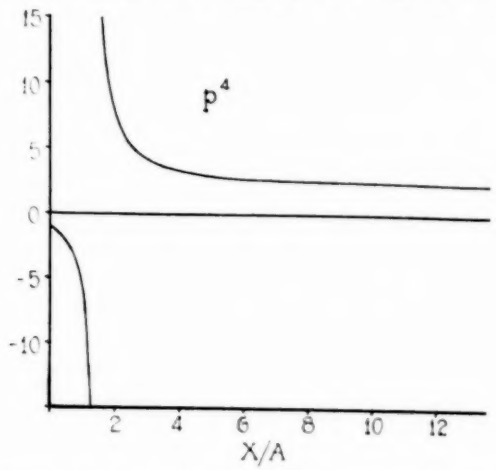

Fig. 2. Interval ratio for $p^4\ ^3P$ for change from (j,j) to Russell-Saunders coupling.

let in cases near the Russell-Saunders coupling. In such an extreme one may take for A one third of the observed total triplet. The triplet intervals must be known with accuracy however and it is therefore impossible to do this in the very important case of the oxygen spectrum. Assuming the interpretation of the auroral line to be correct, we can predict the position of the singlets with respect to the triplet and find (this time referred to the lowest level $^3P_0$):

$$^1D_2 = 11984 \quad ^1S_0 = 29909$$

which is very near the estimate of McLennan and Crawford.[10]

[8] J. C. McLennan and M. F. Crawford, Nature **124,** 874 (1929).

[9] As was said above one can check the formulas in such a way as to make them come out either in good or rather bad agreement with the experiments. The way it is done here, however, is probably the least objectionable, being between the two.

[10] They give 10587 and 28512 which again proves that for predictions of this kind the intuition of an experienced spectroscopist is at least as good as any formula. Nature **124,** 874 (1929).

The configuration p^2. Figures 3 and 4 give the result for this configuration. As was to be expected it differs from p^4 only in the sign[11] of the coefficients of A. Here there is not such an interesting crossing over of levels as in the p^4 case. The total triplet distance is the same in both extreme couplings, but in between it is somewhat *larger*, which is the remarkable fact discovered by Sawyer and Humphreys.[12] It does not check, however, quantitatively.

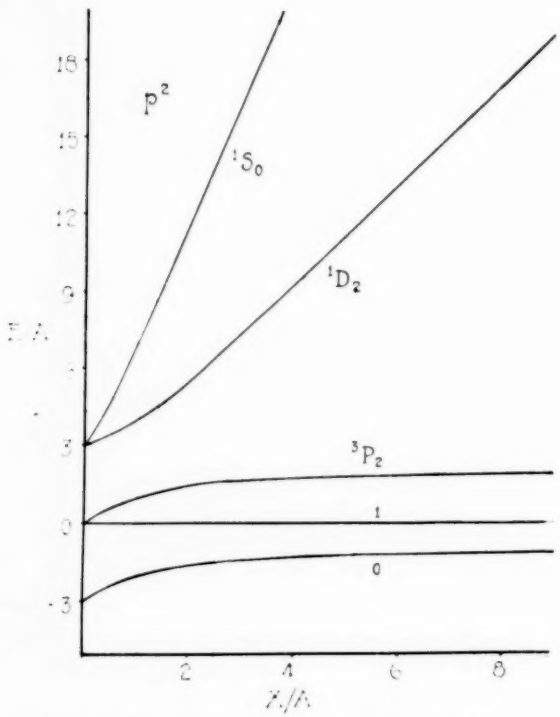

Fig. 3. Change in coupling for configuration p^2

We find a good fitting example in Sn I. By the same method used in the example for p^4 one obtains:

$J = 0$	calc.	-1633	obs. -1692
		$+15412$	$+15471$
$J = 2$		$+1649$	$+1736$
		$+7008$	$+6921.$

The configuration p^3. This configuration gives one level with $J = 2\frac{1}{2}$ one with $J = \frac{1}{2}$ and three with $J = 1\frac{1}{2}$. In the extreme Russell-Saunders coupling they

[11] It might perhaps have been better to take A negative in the case of p^4 and then the formulas for both cases would have been identical.

[12] R. A. Sawyer and C. J. Humphreys, Phys. Rev. **32,** 582 (1928). The explanation which I suggested at that time and which is mentioned in that article is now of course to be considered as pure nonsense.

form a ^4S, a ^2D and a ^2P, the first one being the lowest and from Slater's paper we obtain that their distances are in the ratio 3:2. From the theory of multiplet separations[5] we know that in the ideal case the ^2D and ^2P would show no multiplet splitting at all. For the extreme (j, j) coupling we find[13] a lowest level with $J=1\frac{1}{2}$, a distance $3A$ higher we find three levels with $J=\frac{1}{2}, 1\frac{1}{2}$ and $2\frac{1}{2}$. Finally again $3A$ higher there is the third level with $J=1\frac{1}{2}$. We will choose the level with $J=2\frac{1}{2}$ as reference level. For the level with $J=\frac{1}{2}$ we

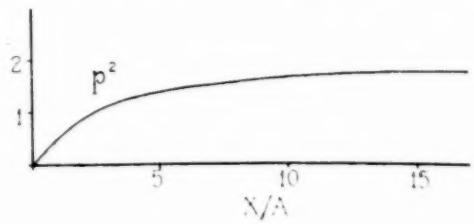

Fig. 4. Interval ratio of $p^2\ ^3P$ for different strengths of coupling.

expect a linear equation but for the three levels with $J=1\frac{1}{2}$ we must have a cubic equation. Writing down these equations with unknown coefficients gives us:

$$\begin{aligned} J &= 2\tfrac{1}{2}: E_{2\frac{1}{2}} = 0 \\ J &= \tfrac{1}{2}\ : E_{\frac{1}{2}} = pX + qA \\ J &= 1\tfrac{1}{2}: E_{1\frac{1}{2}}{}^3 + E_{1\frac{1}{2}}{}^2(aX + bA) + E_{1\frac{1}{2}}(cX^2 + dXA + eA^2) \\ &\quad + fX^3 + gX^2A + hXA^2 + iA^3 = 0. \end{aligned} \tag{4}$$

It is easily found that the coefficient q for $E_{\frac{1}{2}}$ must be 0. With regard to Slater's result we will most conveniently choose $p=2$. For $J=1\frac{1}{2}$ we have the following known roots:

$$\begin{aligned} X = 0: &\quad E_{1\frac{1}{2}} = -3A, 0, +3A. \\ X = \text{large}: &\quad E_{1\frac{1}{2}} = -3X, 0, 2X, \text{ from Slater's results.} \end{aligned}$$

This gives

$$\begin{aligned} i &= 0, \quad b = 0, \quad e = -9; \\ f &= 0, \quad a = 1, \quad c = -6. \end{aligned}$$

We still can determine two more coefficients by remembering that the doublets in the extreme Russell-Saunders case must have zero separation. This means that their levels must fall together even if we take the first order terms of A into account for large X. From this it follows that

$$d = 0 \quad \text{and} \quad g = 0.$$

I see no way, however, to find the coefficient h by the method used here. The final equations are thus

[13] Pauling and Goudsmit, reference 6, 256.

$$
\begin{aligned}
&J = 2\tfrac{1}{2}: E_{2\frac{1}{2}} = 0 \\
&J = \tfrac{1}{2} \ : E_{\frac{1}{2}} = 2X \\
&J = 1\tfrac{1}{2}: E_{1\frac{1}{2}}{}^3 + XE_{1\frac{1}{2}}{}^2 - (6X^2 + 9.1^2)E_{1\frac{1}{2}} + hX.1^2 = 0.
\end{aligned} \tag{5}
$$

The first coefficients tell us that the sum of the levels with $J=1\frac{1}{2}$ is half the distance of the level with $J=\frac{1}{2}$, all referred to $E_{2\frac{1}{2}}$. In As for instance we find $E_{\frac{1}{2}}=7271=2X$ and the sum for $J=1\frac{1}{2}$ is 3580 which indeed checks very well.[14] No good agreement can be found in Bi and in N, in the former case A and in the latter X is probably too large for a first order perturbation calculation to be sufficient.

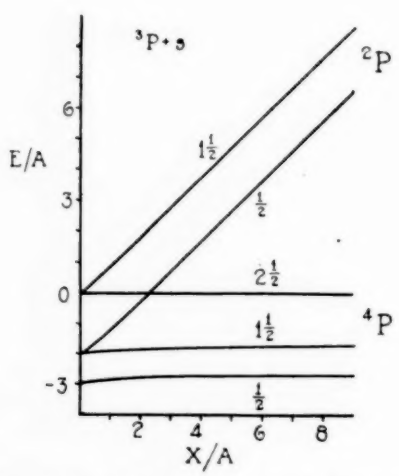

Fig. 5. Addition of an s-electron to a ^3P-state for different strengths of coupling.

The configuration ^3P+s and similar ones. It sometimes occurs that an electron is added to a very regular multiplet state of the next ion for which the connected multiplets of the same configuration are far away. Under such circumstances one may sometimes consider this multiplet as a state in itself and neglect the presence of the other states of the configuration. For such cases we can derive expressions for the variation of the levels with coupling, if we assume that the multiplet state to which the electron is added does not change at all. We will demonstrate this with the simplest example, a ^3P state with an added s-electron. In the extreme (j, j) coupling we find the triplet itself, slightly split up by the addition of the electron, as shown at the left of Figure 5. The total triplet separation we put equal to $3A$. In the extreme Russell-Saunders coupling we obtain a ^4P and a ^2P. The theory of multiplet separations[15] tells us that the separations in the quartet are $5/3\ A$ and A, and the doublet separation is $2A$. With the method described before one now finds, choosing the level with $J=2\frac{1}{2}$ for reference, the following equations:

[14] As the doublets in this example are small it proves Slater's relations rather than our formulas.

[15] For this case see S. Goudsmit and C. J. Humphreys, Phys. Rev. **31**, 960 (1928).

$$
\begin{aligned}
&J = 2\tfrac{1}{2}: E_{2\frac{1}{2}} = 0 \\
&J = 1\tfrac{1}{2}: E_{1\frac{1}{2}}^2 - (X - 2A)E_{1\frac{1}{2}} - 5/3AX = 0 \\
&J = \tfrac{1}{2} : E_{\frac{1}{2}}^2 - (X - 5A)E_{\frac{1}{2}} - 8/3AX + 6A^2 = 0.
\end{aligned} \tag{6}
$$

Though these formulas may give the qualitative change very well, one can hardly expect a quantitative agreement except perhaps in a few extreme cases. Sb I is an example where the ^2P overlaps partially with the ^4P as shown in the left of Fig. 5.

It is not difficult to obtain the formulas for the addition of an s-electron to any multiplet, but if a p- or d- electron is added, it becomes much more complicated.

The configurations d^2 and d^8. As final examples in this paper we shall give the results for these configurations. They can be treated simultaneously and will differ in the sign of A, which will be positive for d^2 and negative for d^8. The levels arising from these configurations are

two	with	$J=4$
one	with	$J=3$
three	with	$J=2$
one	with	$J=1$
two	with	$J=0$.

We shall use the single level with $J=3$ as reference level. In the extreme Russell-Saunders coupling one finds ^3F, ^3P, ^1G, ^1D, ^1S. The distances of the centers of gravity of the various multiplets in the extreme Russell-Saunders coupling from the center of gravity of the ^3F, to which our reference level belongs, will be denoted by

$$
\begin{aligned}
^3F \text{ to } ^3P &= \alpha X \\
^1G &= \beta X \\
^1D &= \gamma X \\
^1S &= \delta X.
\end{aligned}
$$

From Slater's results one obtains among the coefficients the following relations (for d^2 only):

$$
\begin{aligned}
\alpha &= 15 - 15t \\
\beta &= 12 + 2t \\
\gamma &= 5 + 9t \\
\delta &= 22 + 27t.
\end{aligned} \tag{7}
$$

In these expressions t is a new parameter, which from Slater's estimates is about 1/4. Slater showed for this configuration that the coupling energy depended upon two integrals, which will be different from case to case. These two integrals determine our coefficients. In d^8 and many other configurations more integrals enter combined in such a complicated way that no simple relations between the coefficients exist.

To determine as many coefficients as possible in our final formulas we must again take into account the first approximation in A for large X. This means that though the multiplets are far apart, we do not neglect their own splitting up, which, by the way, we know exactly from multiplet separation theory. We take the doublet separation for a single d-electron equal to $5A$. The total separation for the ^3F in the extreme Russell-Saunders coupling is then $7A$, and for the ^3P it is $3A$. Remembering that the distances expressed in X are between the centers of gravity one finds the following energies in the extreme cases:

$$\begin{aligned}
&J = 3: && E_3 = 0, \text{ reference level.}\\
&J = 0: X = 0: && E_0 = 5A,\ -5A\\
&\qquad X \text{ large:} && \qquad (\alpha X - A),\ (\delta X + A)\\
&J = 1: && E_1 = \alpha X\\
&J = 2: X = 0: && E_2 = 0,\ +5A,\ -5A\\
&\qquad X \text{ large:} && \qquad -3A,\ (\alpha X + 2A),\ (\gamma X + A)\\
&J = 4: X = 0: && E_4 = 0,\ +5A\\
&\qquad X \text{ large:} && \qquad +4A,\ (\beta X + A).
\end{aligned}$$

The following expressions are the final results. One sees again that one coefficient in the cubic equation for $J=2$ could not be determined by our method.

$$\begin{aligned}
&J = 3: E_3 = 0\\
&J = 0: E_0^2 - (\alpha + \delta)XE_0 + \alpha\delta X^2 + (\alpha - \delta)XA - 25A^2 = 0\\
&J = 1: E_1 = \alpha X\\
&J = 2: E_2^3 - (\alpha + \gamma)XE_2^2 + [\alpha\gamma X^2 - (2\alpha + \gamma)XA - 25A^2]E_2\\
&\qquad + 3\alpha\gamma X^2A + hXA^2 = 0\\
&J = 4: E_4^2 - (\beta X + 5A)E_4 + 4\beta XA = 0
\end{aligned} \tag{9}$$

The Zeeman Effect

The application of an external magnetic field may be treated by the addition of a perturbation parameter to our formulas. We denote the field strength by H, expressed in the right units so as to obtain wave numbers in our equations.[16] We then add terms with H to all our coefficients, but as we are only interested in the results for weak fields, we need consider the terms in the first power[17] of H only. We shall discuss the simple case in which the energy is given by a quadratic equation. One can easily extend it to more

[16] For this purpose the wave-number shift of the normal Zeeman effect must be chosen as the unit.

[17] Taking into account all the powers of H would lead to the study of the Paschen-Back effect, which has been done in great detail by C. G. Darwin, Proc. Roy. Soc. **A115,** 1 (1927).

complicated cases but it is then in general impossible to determine all the necessary coefficients by our method. Equation (1) we will now write

$$E^2 + E(x + pH) + y_2 + qzH = 0. \tag{10}$$

In this equation x, y_2 and z stand symbolically for the linear and quadratic functions of the other perturbations, such as X and A. We assume that x and y_2 are completely known from the problem without field. The term in H^2 has been purposely omitted. We know that the field splits each level into a number of levels with different values of the magnetic quantum number M, but for our purpose we consider only an arbitrarily chosen value for this number. If E' and E'' were the energy levels without field, they become in the field

$$E = E' + Mg'H \text{ and } E'' + Mg''H.$$

Substituting these values in (10) leads at once to

$$g' = -\frac{pE' + qz}{2E' + x} \text{ and } g'' = -\frac{pE'' + qz}{2E'' + x}. \tag{11}$$

There originally stood Mg' and Mg'', but just because M enters here merely as a proportionality factor we can put it equal to 1 irrespective of the fact whether this is an in reality possible value for M or not. From the first part of this paper we have

$$x = -E' - E''.$$

Substituting this and adding the two g-values shows

$$g' + g'' = -p. \tag{12}$$

This is the well-known g-sum rule for this simple case and it tells us at once the value of the coefficient p. The coefficients q of the linear function z of the other perturbation parameters has not such a simple meaning but can always be found by means of the known g-values in extreme couplings.

In our example of the configuration p^4 we find for instance

$$\text{for } J = 2 \qquad g = \frac{5/2E - 3X + 7/2A}{2E - 2X + 3A} = \frac{5/2E' - 3X + 7/2A}{E' - E''}. \tag{13}$$

For p^2 one obtains again the same formulas but with the sign of A reversed.

Conclusion

We have illustrated our method of deriving relations between multiplets by various examples. Needless to say it is possible to apply it to many more cases than have been mentioned here. For instance it is clear that the formulas derived by Houston can be easily obtained by our method.

In a following paper a few more cases will be treated and the formulas will be applied to the available spectroscopic material. It is actually surprising

that in many instances they are not so very bad after all and even the discrepancies may prove to be of interest.[18]

The intensities can be treated by a similar procedure as used in this paper especially since we now know the intensity formulas for the extreme (j, j) coupling from the recent paper by Bartlett.[19]

This and the following paper, I hope, will contribute a little bit to the understanding of spectra with intermediate coupling. The fact that so few of such spectra have been analysed at present is certainly only due to a lack of theoretical knowledge of their structure, for the classification of these spectra can not be so very much harder than for multiplet spectra. But one must not look for multiplets in spectra where there are not such structures and one perhaps ought to start by abolishing the use of multiplet notations in those cases, where they are, in the main, meaningless and misleading.

[18] Compare a paper by Laporte and Inglis treating important examples of the d^9s and p^5s configurations, as was mentioned at the beginning of this article. This issue, p. 1337.

[19] J. H. Bartlett, Phys. Rev. **35,** 229 (1930).

RESONANCE SEPARATIONS IN CONFIGURATIONS OF TYPE p^5s and d^9s

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Abstract

Considerations concerning the invariance of the configurations p^5 and d^9 with changing coupling lead to application of Houston's formulas to the cases p^5s and d^9s with negative A and X values. The expressions thus obtained are tested on the separations and g values of numerous spectra. The agreement is satisfactory.

As IS well known the separations of the levels within a configuration depend upon influences of two kinds: firstly those of relativistic origin obeying a $(Z-\sigma)^4$ law and secondly those depending upon the coupling between the electrons. Although through the researches of Goudsmit[1] and Slater[2] the niveau distances are known in the extreme cases of pure Russell-Saunders and of pure $\{jj\}$ coupling, the transition stage has heretofore been investigated only for simple configurations of two electrons one of which is in an s state. The formulas of this case were given by Houston.[3]

For pure $\{LS\}$ coupling such a configuration yields a triplet and a singlet term with inner quantum numbers $l-1, l, l+1$ and l; the total separation of the triplet term which is given by the Sommerfeld formula

$$\frac{\Delta\nu}{R} = \frac{\alpha^2(Z-\sigma)^4}{n^3 l(l+1)} \tag{1}$$

is small compared with the distance between the two terms. Here A denotes the so-called interval factor, n and l are the quantum numbers of that electron which is not in the s state; Z is the nuclear charge, σ the screening number and $R\alpha^2$ a universal constant with the value 5.82. The position of the middle triplet level is fixed by Landé's interval rule.

In the other extreme case of pure $\{jj\}$ coupling the four levels are arranged in two narrow doublets with the distance (1) from each other. All one knows from elementary considerations about the transition is that the change in coupling will not affect the distance between levels whose inner quantum numbers occur only once, like $l-1$ and $l+1$.

If we define the centroid of the triplet term in the well-known way by

$$\Gamma(J) = \tfrac{1}{2}A(J(J+1) - l(l+1) - 2),$$

then the general formulas of Houston for the transition from $\{LS\}$ to $\{jj\}$ coupling may be written:

[1] S. Goudsmit. Phys. Rev. **31,** 946 (1928).
[2] J. C. Slater, Phys. Rev. **34,** 1293 (1929).
[3] W. V. Houston, Phys. Rev. **33,** 297 (1929).

$$\left.\begin{aligned} \Gamma_1(l) &= A\left\{\frac{X-1}{2}+\frac{1}{2}((X+1)^2+4l(l+1))^{1/2}\right\} \\ \Gamma(l+1) &= Al \\ \Gamma_2(l) &= A\left\{\frac{X-1}{2}-\frac{1}{2}((X+1)^2+4l(l+1))^{1/2}\right\} \\ \Gamma(l-1) &= -A(l+1) \end{aligned}\right\} \tag{2}$$

X is the parameter which describes the transition; for $X=\infty$ we obtain pure $\{LS\}$, for $X=0$ pure $\{jj\}$ coupling.

Modification of Houston's Formulas

The application of these formulas to configurations of type p^5s and d^9s suggested itself to the authors for two reasons: firstly the inner quantum numbers are the same as in the cases ps and ds, and secondly it follows from the above mentioned considerations of Goudsmit, that the configurations p^5 and d^9 yield regardless of coupling ^2P and ^2D terms the separation of which is given by (1). The only difference is that these terms possess a negative A value, *i.e.* they are inverted. In (2) a negative A value would mean that (for large X) the singlet lies below the triplet term—which is almost never the case. Upon changing the sign of X also, it is seen however that the singlet term and the middle triplet level change places. Thus a negative X as well as a negative A brings about the desired arrangement with an inverted triplet term and a singlet level above it. If then $-X=X'$ and $-A=A'$ with X', $A'>0$ are introduced into (2) we obtain:

$$\left.\begin{aligned} \Gamma_2(l) &= A'\left\{\frac{X'+1}{2}+\frac{1}{2}((X'-1)^2+4l(l+1))^{1/2}\right\} \\ \Gamma(l-1) &= A'(l+1) \\ \Gamma_1(l) &= A'\left\{\frac{X'+1}{2}-\frac{1}{2}((X'-1)^2+4l(l+1))^{1/2}\right\} \\ \Gamma(l+1) &= -A'l. \end{aligned}\right\} \tag{3}$$

For positive X' the magnitude of the four Γ values is in the order in which they are given above. It is readily seen that for large or small X' values, that is to say complete $\{LS\}$ or complete $\{jj\}$ coupling, the levels have indeed the position required.

All that has been said about the separations holds *mutatis mutandis* for the g values of the Zeeman effect. Due to the principle of the permanency of the g sums the g values of the outer triplet levels (with inner quantum numbers $l\pm1$) are independent of the coupling. They remain unaltered and thus offer nothing new. The g values of the middle triplet level and the singlet level however are obtained from Houston's expressions by introducing $-X=X'>0$. Thus the following formulas are arrived at:

$$\left.\begin{aligned} g_2(l) &= 1 + \frac{1}{2l(l+1)} + \frac{X'-1}{2l(l+1)((X'-1)^2+4l(l+1))^{1/2}} \\ g_1(l) &= 1 + \frac{1}{2l(l+1)} - \frac{X'-1}{2l(l+1)((X'-1)^2+4l(l+1)]^{1/2}} \end{aligned}\right\} \quad (4)$$

Comparison With Data

A vast amount of spectroscopic material can be interpreted by means of the equations (3), because levels of type p^5s and d^9s occur in a series of well investigated spectra of rare-gas type and of Ni, Pd and Pt type.[4] Fortunately these spectra have lost their Russell-Saunders character almost completely. The comparison with the data was carried out in the following manner. First from the distance $\Gamma(l-1)-\Gamma(l+1)=A'(2l+1)$ the values of A' were obtained. Then by means of the second and fourth equation (3) the position of the centroid was determined. Finally two independant values of X' were calculated from Γ_2 and Γ_1 by means of the formula

$$X'_{1,2} = \frac{\Gamma_{1,2}}{A'} - \frac{l(l+1)}{(\Gamma_{1,2}/A') - 1} \quad (3')$$

in order to avoid giving preferance to either level. The agreement of these two determinations is a measure for the degree of accuracy with which (3) represent the measured separations.

The following Tables I and II give the numerical values for the levels of type p^5s and d^9s respectively. The first and second columns contain symbols

Table I.

Spectrum	Configuration	$^1P_1-{}^3P_0$	$^3P_0-{}^3P_1$	$^3P_1-{}^3P_2$	A'	X_2	X_1	g_2	g_1
Ne I	$2p^53s$	1070.1	359.3	417.4	258.9	5.75	5.78	1.036	1.464
Ne I	$2p^54s$	153.7	584.0	194.8	259.6	1.33	1.35	1.220	1.280
Ne I	$2p^55s$	50.1	693.6	84.6	259.1	0.53	0.53	1.291	1.209
Ne I	$2p^56s$	21.7	738.6	42.7	260.4	0.24	0.25	1.314	1.186
Ne I	$2p^511s$	3.28	775.5	4.70	260.1	0.04	0.03	1.331	1.169
Na II	$2p^53s$	2481.0	592.0	765.5	452.8	7.17	7.14	1.023	1.477
Mg III	$2p^53s$	3688	977	1216	731	6.86	6.60	1.026	1.464
A I	$3p^54s$	846.2	803.1	606.8	470.0	3.09	3.11	1.101	1.399
A I	$3p^56s$	64.7	1236.5	77.1	471.2	1.56	0.25		
A I	$3p^57s$	9.23	1393.7	48.3	477.7	0.05	0.12		
A I	$3p^58s$	18.5	1452.5	−21.0	473.0	0.13	−0.07		
A I	$3p^59s$	8.61	1420.2	11.1	473.1	0.03	0.08		
K II	$3p^54s$	1312.0	1912.5	730.0	880.8	2.69	1.54	1.16	1.34
K II	$3p^55s$	291.8	1734.1	417.4	716.8	0.99	0.99	1.251	1.249
Ca III	$3p^54s$	1985.0	1681.4	1383.5	1021.7	3.38	3.45	1.087	1.413
Ca III	$3p^55s$	355.9	2462.3	563.4	1041.9	0.85	1.10	1.252	1.248
Kr I	$4p^55s$	655.0	4274.9	945.0	1740.0	0.920	0.915	1.257	1.243
Xe I	$5p^56s$	988.3	8141.6	977.6	3043.1	0.80	0.51	1.281	1.219

[4] The sources of data on the Ni-, Pd-, and Pt-like spectra are listed in a paper by J. E. Mack, Phys. Rev. **34,** 18 (1929). Other sources are: Cu: G. Kruger; Phys. Rev. **34,** 1122 (1929). Ne: F. Paschen and R. Goetze, Seriengesetze der Linienspektren, 1922. Na: O. Laporte, Nature **121,** June 16 (1928). Mg: J. E. Mack and R. A. Sawyer, Science **68,** 306 (1928). A: K. W. Meissner, Zeits. f. Physik **39,** 172 (1926); **40,** 839 (1926). K, Ca: I. S. Bowen, Phys. Rev. **31,** 497 (1928). Kr: W. F. Meggers, T. L. de Bruin, C. J. Humphreys, B. S. Journ. Res. **3,** 129 (1929).

for the spectra and configurations in question. In the third, fourth and fifth columns the separations of the four levels are given in cm^{-1}. The sixth column contains the values of the interval factor A'. The seventh and eighth columns

TABLE II.

Spectrum	Configuration	$^1D_2-^3D_1$	$^3D_1-^3D_2$	$^3D_2-^3D_3$	A'	X_2	X_1	g_2	g_1
Ni I	$3d^94s$	1696.8	833.3	675.0	301.66	7.90	8.12	1.015	1.152
Ni I	$3d^95s$	150.4	1322.2	184.1	301.26	1.06	1.11	1.082	1.085
Cu II	$3d^94s$	2266.0	1151.2	918.5	413.94	7.73	8.02	1.015	1.151
Cu II	$3d^95s$	281.7	1748.7	320.9	413.9	1.44	1.38	1.077	1.090
Cu II	$3d^96s$	95.7	1935.7	133.9	413.9	0.54	0.57	1.091	1.076
Cu II	$3d^97s$	51.1	2001.6	69.6	414.2	0.29	0.29	1.095	1.071
Zn III	$3d^94s$	2650	1576	1178	551	6.93	7.09	1.018	1.148
Ga IV	$3d^94s$	2937	2120	1455	715	6.14	6.26	1.022	1.027
Ge V	$3d^94s$	3180	2796	1740	907	5.42	5.46	1.027	1.139
Pd I	$4d^95s$	1627.8	2338.9	1191.0	706	3.92	4.26	1.051	1.115
Ag II	$4d^95s$	2306.5	3017.7	1557.1	915	4.89	4.32	1.034	1.132
Cd III	$4d^95s$	2652.4	3866.0	1900.1	1153.2	3.91	4.08	1.040	1.127
In IV	$4d^95s$	2871	4912	2196	1422	3.51	3.67	1.044	1.122
Sn V	$4d^95s$	3025	6142	2478	1724	3.15	3.27	1.049	1.117
Pt I	$5d^96s$	3364.3	9356.1	775.9	2026	2.96	0.73		
Au II	$5d^96s$	1855.3	10125.2	2601.5	2545.3	1.53	2.05	1.070	1.096
Hg III	$5d^96s$	2679	12377	3179	3111	1.76	2.05	1.068	1.098
Tl IV	$5d^96s$	2916	15277	3588	3773	1.56	1.87	1.071	1.127

give the two values of X' as calculated from (3′), and finally in the ninth and tenth columns the g values are listed which were computed from (4) using an average X'.

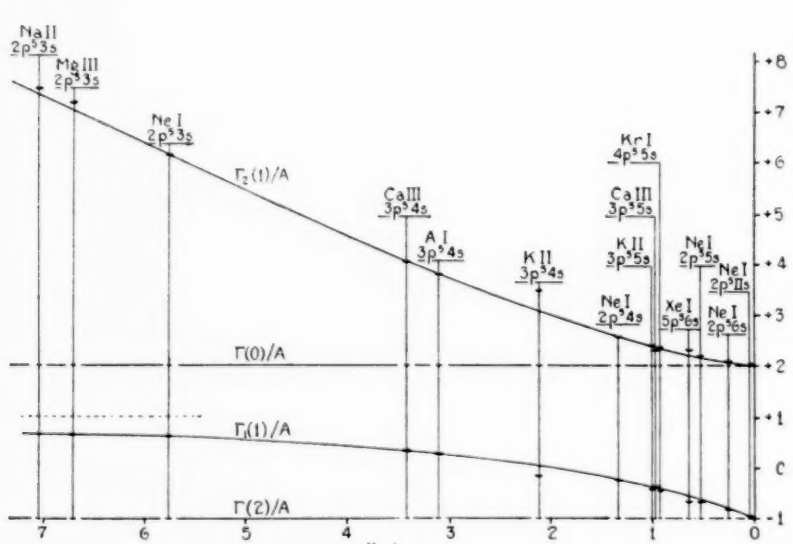

Fig. 1. Values of Γ/A' plotted against X'.

In Fig. 1 and 2 the values of Γ/A' are plotted against X' for the configurations p^5s and d^9s. Obviously by dividing with A' we free ourselves of the dependance upon the spin doublet of the preceding ion and are then in a position to study the dependence of the separations upon X' alone.

The bad agreement in the case of platinum is probably due to the fact that our equations (3) which are only the result of a first order calculation do not hold in the case of very large A' values which are comparable with the ionization potential d^9s-d^9. We thus understand the better agreement for the higher isoelectronic analogues of Pt I, namely Au II, Hg III, etc.

On the other hand the total lack of agreement for the higher series members $3p^5 6s$ to $3p^5 9s$ of A I renders doubtful the identifications of the combinations involved. The same might be said of $3p^5 4s$ of K II.

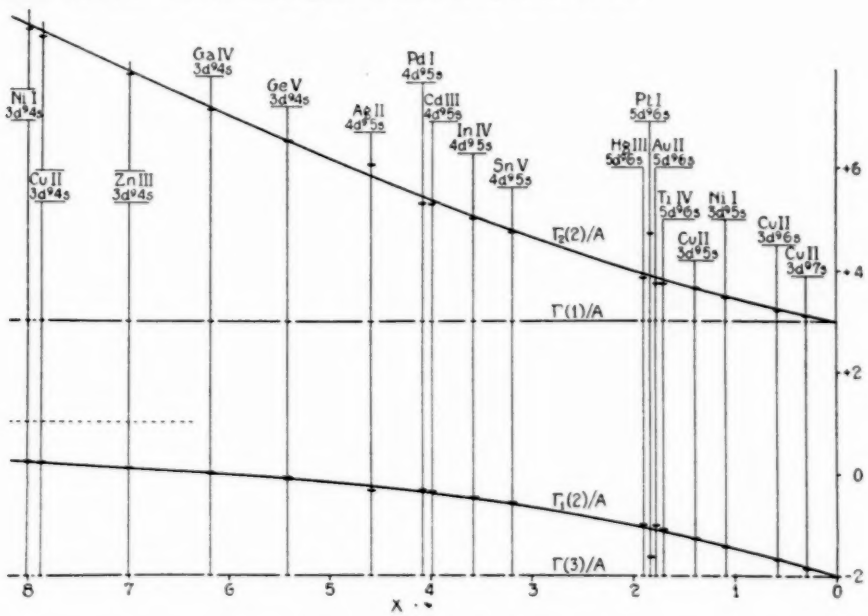

Fig. 2. Values of Γ/A' plotted against X'.

It is interesting to study the dependence of X' upon Z for a group of isoelectronic spectra. It seems that after some initial irregularities X' varies almost linearly with Z.

The only spectrum in which a comparison of the equations (4) with the experiment is possible, is Ne I. In this spectrum the g values of the singlet and the middle triplet level of $2p^5 3s$ were measured by Back.[5] The following Table III gives the comparison of experimental and theoretical values.

TABLE III.

	observed (Back)	calculated Table II.	calculated $\{LS\}$ coupling	calculated $\{jj\}$ coupling
g_2	1.034	1.036	1.000	1.300
g_1	1.464	1.464	1.500	1.200

The agreement is excellent. Many attempts have been made in the past to compute the g values of these Ne levels, but naturally only the values in limiting cases were obtained.

[5] E. Back, Ann. d. Physik **76**, 329 (1925).

SINGLET-TRIPLET INTERVAL RATIOS FOR *sp*, *sd*, *sf*, p^5s AND d^9s CONFIGURATIONS*

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(Received April 29, 1930)

Abstract

A systematic comparison of the known data on the singlets and triplets arising from *sp*, *sd*, *sf*, p^5s and d^9s configurations with the theory of Houston shows that the theory gives a good account of the deviations from the Landé interval rule which accompany departure from Russell-Saunders coupling. There are numerous significant discrepancies, however. Writing ${}^1L_l$ and ${}^3L_{l+1}$, ${}^3L_l$, ${}^3L_{l-1}$ with $L=P, D, F$, when $l=1, 2, 3$ for the term values, we plot as abscissa $({}^3L_{l-1}-{}^3L_{l+1})/|{}^3L_l-{}^1L_l|$ and $({}^3L_{l-1}-{}^3L_l)/({}^3L_l-{}^3L_{l+1})$ as ordinate if $({}^3L_l-{}^1L_l)$ is positive, otherwise the reciprocal of this quantity. Houston's equations (12) give functional relations between these interval ratios which are compared with the experimental values.

HOUSTON[1] has worked out an approximate quantum mechanical theory of the relation of the triplet interval ratio to the singlet-triplet interval for two electron configurations in which one of the electrons is in an *s* state, but the comparison he makes with experimental data gives one very little idea as to just how accurate the theory is. The purpose of the present paper is therefore to make a systematic comparison of the available data with Houston's theory.

If we write the terms of a singlet-triplet system as ${}^1L_l$, ${}^3L_{l+1}$, ${}^3L_l$, ${}^3L_{l-1}$, with $L=P, D, F$, when $l=1, 2, 3$, Houston's equations (12) give the following relative term values in terms of the parameter X, which is the ratio of the exchange perturbation integral to the perturbation theory integral which measures the spin energy. (The first classification applies to $X>0$, the second to $X<0$.):

$$\begin{aligned} {}^1L_l, {}^3L_l &= -\tfrac{1}{2}(X-1) - \tfrac{1}{2}\{(X+1)^2 + 4l(l+1)\}^{1/2} \\ {}^3L_{l+1} &= -l \\ {}^3L_l, {}^1L_l &= -\tfrac{1}{2}(X-1) + \tfrac{1}{2}\{(X+1)^2 + 4l(l+1)\}^{1/2} \\ {}^3L_{l-1} &= l+1. \end{aligned}$$

Fig. 1. illustrates the behavior of these intervals. With X large and positive the triplet has the Landé interval and the singlet is high above the triplet as at a. As X approaches zero the levels approach coincidence in pairs as at b; and with X large and negative we again have the Landé interval with the singlet far below the triplet as at c.

* This paper was presented at the Washington meeting of the American Physical Society, April 24, 1930.

[1] W. V. Houston, Phys. Rev. **33**, 297 (1929).

The theoretical curves of Figs. 2 and 3 are plotted as follows: For abscissa is used $({}^3L_{l-1}-{}^3L_{l+1})/|{}^3L_l-{}^1L_l|$. For the lower curve, $X>0$, the ordinate is $({}^3L_{l-1}-{}^3L_l)/({}^3L_l-{}^3L_{l+1})$, which goes from $l/(l+1)$ with abscissa zero, to zero with abscissa one. For the upper curve, $X<0$, the ordinate

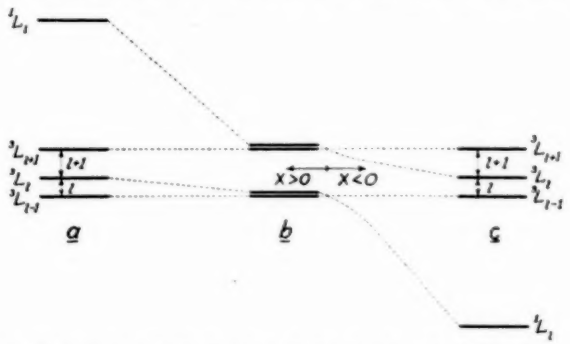

Fig. 1. Diagram illustrating the behavior of the singlet-triplet intervals. (*a*) X large and positive. (*b*) X very small and positive. (*c*) X large and negative.

is the reciprocal of this, $({}^3L_l-{}^3L_{l+1})/({}^3L_{l-1}-{}^3L_l)$, which goes from zero with abscissa one to $(l+1)/l$ with abscissa zero. The fact that the abscissa starts increasing (to $(l+\frac{1}{2})/(l(l+1))^{1/2}$ at $X=-1$) shows that ${}^1L_l-{}^3L_l$ becomes less than the whole spread of the triplet until the ordinate equals $1/2l$ at $X=-2$.

TABLE I. *Coordinates.*

† indicates a point which is not plotted on account of large probable error (see text).
• indicates a point which does not fall within the limit of Figs. 2 and 3.

Elem.	Config.	$sp(X>0)$ Abs.	Ord.	Sources
Al II	$3s3p$	0.0084	0.493	Int. Crit. Tab.
	$4p$	0.0293	0.481	
	$5p$	0.1145	0.445	
Ba I	$6s6p$	0.2301	0.422	Int. Crit. Tab.
	$7p$	0.1410	0.420	
	$8p$	0.1181	0.619	
C I	$3s2p$	0.0527	0.499	Proc. Roy. Soc. **A118,** 43
Ca I	$4s4p$	0.0179	0.494	Int. Crit. Tab.
	$5p$†	0.1253	0.110	
Cd I	$5s5p$	0.1315	0.462	Int. Crit. Tab.
	$6p$	0.1695	0.406	
	$7p$	0.202	0.355	
	$8p$	0.211	0.378	
	$9p$	0.219	0.367	
Ga II	$4s4p$	0.0604	0.478	Phys. Rev. **34,** 714
	$5s4p$	0.1476	0.424	
Ge I	$5s4p$	0.719	0.177	Phys. Rev. **31,** 786
	$6s4p$	0.914	0.095	
Ge III	$4s4p$	0.0818	0.465	Phys. Rev. **34,** 698
	$5p$	0.276	0.366	
Hg I	$6s6p$	0.436	0.382	Int. Crit. Tab.
	$7p$	1.035	0.094	
	$8p$	0.952	0.056	
Mg I	$3s3p$	0.0046	0.487	Int. Crit. Tab.
N II	$3s2p$	0.680	0.235	Proc. Roy. Soc. **A114,** 662
	$4s2p$	0.135	0.437	
	$5s2p$	0.305	0.373	
O III	$3s2p$	0.0658	0.458	Proc. Roy. Soc. **A118,** 43
Pb I	$7s6p$	0.972	0.032	Phys. Rev. **33,** 301
Pb III	$6s6p$	0.600	0.274	Phys. Rev. **34,** 397
Sb IV	$5s5p$	0.278	0.388	Phys. Rev. **34,** 402
Si I	$4s3p$	0.221	0.395	Zeits. f. Phys. **40,** 530
Sn I	$6s5p$	0.918	0.074	Phys. Rev. **30,** 574
Sn III	$5s5p$	0.230	0.407	Int. Crit. Tab.
	$6p$	0.598	0.226	
Sr I	$5s5p$	0.0808	0.474	Int. Crit. Tab.
	$6p$	0.607	0.395	
Te V	$5s5p$	0.323	0.366	Phys. Rev. **34,** 402
Tl II	$6s6p$	0.528	0.316	Phys. Rev. **35,** 236
	$7p$	0.403	0.088	
Zn I	$4s4p$	0.0406	0.489	Int. Crit. Tab.
	$5p$	0.0507	0.475	
	$6p$	0.0589	0.464	
	$7p$	0.0666	0.456	
	$8p$	0.0651	0.464	
	$9p$†	0.0739	0.514	
Yt II	$5s5p$	0.321	0.380	Bur. Stand. Jl. of Res. **2,** 738

Elem.	Config.	$sp\ (X<0)$ Abs.	Ord.	Sources
Al II	$3s6p$•	0.1045	2.193	Int. Crit. Tab.
Ca I	$4s6p$	0.0140	1.950	Int. Crit. Tab.
Hg I	$6s9p$•	0.3935	5.356	Int. Crit. Tab.
	$10p$•	0.1273	7.135	
	$11p$•	0.1131	8.73	
Sr I	$5s7p$•	0.0902	2.100	Int. Crit. Tab.

Elem.	Config.	$p^2s\ (X<0)$ Abs.	Ord.	Sources
A I	$3p^24s$	0.854	0.756	Zeits. f. Phys. **40,** 839
	$6s$	1.008	0.0578	
	$7s$	1.021	0.0282	
	$9s$	1.002	0.0078	
Ca III	$3p^24s$	0.814	0.823	Phys. Rev. **31,** 501
	$5s$•	1.109	0.269	
K II	$3p^24s$	0.819	0.383	Phys. Rev. **31,** 501
	$5s$	1.063	0.241	
Kr I	$4p^25s$	1.058	0.221	B. S. Jl. Res. **3,** 154
Na II	$2p^23s$	0.442	1.293	Phys. Rev. **31,** 967

TABLE I (*continued*)

Ne I	$2p^5 3s$	0.544	1.161	Int. Crit. Tab.
	$5s$	1.047	0.122	
	$6s$	1.027	0.0578	
	$7s$	1.017	0.0322	
	$8s$	1.010	0.0211	
	$9s$	1.006	0.0125	
	$10s$	1.003	0.0084	
	$11s$	1.001	0.0061	
Xe I	$5p^5 6s$	0.999	0.120	B. S. Jl. Res. **3**, 756

sd ($X>0$)

Elem.	Config.	Abs.	Ord.	Sources
Ba I	$6s5d$	0.258	0.476	Int. Crit. Tab.
Ca I	$4s3d$	0.0237	0.640	Int. Crit. Tab.
	$5d$†	0.0258	0.607	
	$7d$†	0.712	0.750	
Cr V	$4s3d$	0.1678	0.525	Phys. Rev. **33**, 542
Lu II	$6s5d$	0.490	0.363	Bul. Am. Ph. Soc. Apr. 10, 1930, 11
[5]Pb III	$6s5d$	0.220	0.466	Phys. Rev. **34**, 397
Sb IV	$5s5d$	0.258	0.628	Phys. Rev. **34**, 402
	$6d$	0.562	0.683	
Sc II	$4s3d$	0.0718	0.616	Sci. Papers, Bur. Stand. **22**, 329
	$5s3d$	0.301	0.483	
Sn III	$5s5d$	0.250	0.659	Int. Crit. Tab.
	$6d$	0.129	0.610	Phys. Rev. **34**, 402
Sr I	$5s4d$	0.083	0.600	Int. Crit. Tab.
	$6d$	0.409	0.398	
Te V	$5s5d$	0.257	0.616	Phys. Rev. **34**, 402
Ti III	$4s3d$	0.1031	0.592	Astro. Jl. **66**, 13
V IV	$4s3d$	0.1335	0.558	Phys. Rev. **33**, 542
Yt II	$5s4d$	0.272	0.506	B. S. Jl. Res. **2**, 738
	$6s4d$	0.996	0.124	

sd ($X<0$)

Elem.	Config.	Abs.	Ord.	Sources
Ba I	$6s6d$	0.0485	1.228	Int. Crit. Tab.
	$7d$	0.0456	0.438	
	$8d$	0.0284	1.190	
	$9d$	0.0716	1.595	
	$10d$†	0.0324	4.61	
Ca I	$4s4d$	0.0207	1.474	Int. Crit. Tab.
	$6d$†	0.0544	1.200	
Cd I	$5s5d$	0.1074	1.555	Int. Crit. Tab.
	$6d$	0.0621	1.414	
	$7d$	0.0553	1.388	
	$8d$†	0.0454	6.000	
Ga II	$4s4d$	0.0096	1.360	Phys. Rev. **34**, 714
	$5s4d$	0.0029	1.416	
	$6s4d$	0.0022	1.125	
Ge III	$4s4d$	0.0099	1.505	Phys. Rev. **34**, 697
Hg I	$6s6d$*	1.510	0.585	Int. Crit. Tab.
	$7d$	1.018	0.923	
	$8d$	0.808	1.051	
	$9d$	0.717	1.438	
	$10d$	0.653	0.556	
[5]Pb III	$6s5d$*	0.250	2.145	Phys. Rev. **34**, 397
Sr I	$5s5d$	0.183	1.520	Int. Crit. Tab.
	$7d$	0.273	1.195	
	$8d$	0.163	1.250	
	$9d$	0.298	1.271	
Tl II	$6s6d$	0.532	1.384	Phys. Rev. **35**, 236
	$7d$	0.237	1.173	
	$8d$*	0.118	1.861	
Zn I	$4s4d$	0.0283	1.618	Int. Crit. Tab.
	$5d$†	0.0128	1.818	
Yt II	$5s5d$	0.0533	1.509	B. S. Jl. Res. **2**, 738

d^9s ($X<0$)

Elem.	Config.	Abs.	Ord.	Sources
Ag II	$4d^9 5s$	0.862	0.526	Phys. Rev. **31**, 317
	$6s$	1.022	0.0896	
Au II	$5d^9 6s$	1.062	0.2569	Phys. Rev. **34**, 19
Cd III	$4d^9 5s$	0.886	0.4916	Phys. Rev. **31**, 778
Cu II	$3d^9 4s$	0.605	0.798	Phys. Rev. **29**, 386
	$5s$	1.018	0.1835	
	$6s$	1.018	0.0692	Phys. Rev. **34**, 1128
	$7s$	1.010	0.0348	
Ga IV	$3d^9 4s$	0.708	0.686	Phys. Rev. **31**, 750
Ge V	$3d^9 4s$	0.759	0.622	Phys. Rev. **31**, 750
Hg III	$5d^9 6s$	1.033	0.2568	Phys. Rev. **34**, 19
In IV	$4d^9 5s$	0.913	0.447	Phys. Rev. **31**, 778
Ni I	$3d^9 4s$	0.596	0.810	Phys. Rev. **29**, 386
	$5s$	1.024	0.1393	
	$6s$	1.016	0.0519	Phys. Rev. **34**, 828
Pd I	$4d^9 5s$	0.890	0.510	Phys. Rev. **29**, 386
	$6s$	1.018	0.065	
Pt I	$5d^9 6s$	0.796	0.0829	Phys. Rev. **34**, 19
	$7s$	1.001	0.0374	Phys. Rev. **34**, 190
Tl IV	$5d^9 6s$	1.042	0.235	Phys. Rev. **34**, 19
Zn III	$3d^9 4s$	0.652	0.748	Phys. Rev. **30**, 381

sf ($X>0$) (not plotted)

Elem.	Config.	Abs.	Ord.	Sources
Al II	$3s4f$†	0.0978	0.750	Int. Crit. Tab.
	$5f$	0.0506	0.783	
	$6f$	0.0573	0.777	
	$7f$	0.0389	0.761	
	$8f$	0.0118	0.657	
	$9f$†	0.0049	0.750	
	$10f$†	0.0030	0.786	
	$11f$†	0.0016	0.667	
	$12f$†	0.0019	0.800	
[6]Ge III	$4s4f$	1.384	0.275	Phys. Rev. **34**, 697
Sn III	$5s4f$	0.0556	0.378	Int. Crit. Tab.
	$5f$	0.0312	0.357	Phys. Rev. **30**, 574
Sr I	$5s4f$†	0.0056	0.630	Int. Crit. Tab.
	$5f$†	0.0113	0.889	
	$6f$†	0.1765	0.049	
	$7f$†	0.314	0.165	

sf ($X<0$) (not plotted)

Elem.	Config.	Abs.	Ord.	Sources
Ba I	$6s4f$	0.0046	1.014	Int. Crit. Tab.
	$5f$	0.0847	4.34	
	$6f$	0.0092	1.594	

[5] S. Smith, Phys. Rev. **34**, 397 (1929) has a question as to which of two singlets belong to this configuration. These are both listed, one for $X>0$, plotted with a question mark and one for $X<0$, which fell off the graph.
[6] The singlet is within the triplet.

A fairly complete search of the literature was made and the points plotted on Figs. 2 and 3. The coordinates are tabulated in the accompanying tables together with a brief reference to the source of the data. No points were plotted for which any of the intervals were less than 2.5 cm^{-1}, since the accuracy of these points did not seem to be sufficient for a fair comparison with the theory. Such points are listed in the table with a dagger (†). Those points

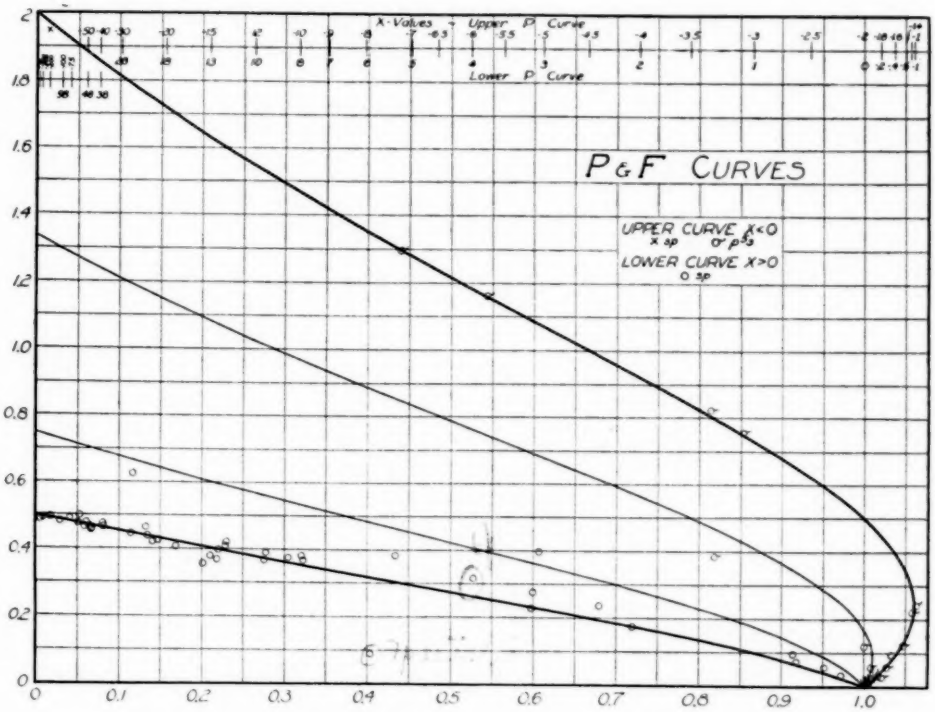

Fig. 2. *P* and *F* curves showing *sp* and p^2s points. (*F* curve is drawn lightly and no points plotted.)

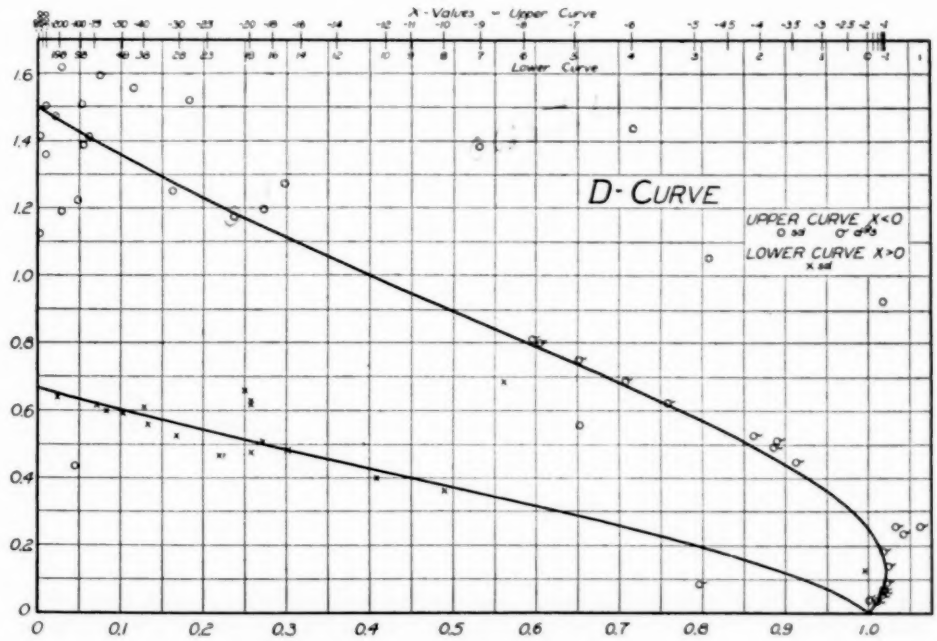

Fig. 3. *D* curve showing *sd* and d^2s points.

whose coordinates fell off the graph are listed with an asterisk (*). No *sf* points were plotted because there were just a few clustered near Russell-Saunders coupling.

It is found that the theory works well for p^5s and d^9s configurations, in which we are one *p* or *d* electron short of a closed shell, except that the whole system of lines is inverted. These points all fall on the upper curves.

Pb III[2] and Tl II[3] have *sf* configurations in which $^3F_3$ and $^1F_3$ are on opposite sides and outside of the $^3F_2-{}^3F_4$ interval. A similar thing happens in the case of the $3p^5\ 8s$ configuration of A I[4]. These partially inverted triplets might have been plotted with negative ordinates on our graphs.

As to the accuracy with which the points fit the theory, it can be said that in general the d^9s and p^5s fit best, *sp* and *sd* for $X>0$ next, and *sp* and *sd* for $X<0$ poorest. Also in general, elements of high atomic number show especially pronounced disagreements. The disagreements are to be regarded provisionally as cases in which the second-order perturbations are not negligible rather than as essential defects in the basic theory.

[2] S. Smith, Phys. Rev. **34,** 397 (1929).
[3] S. Smith, Phys. Rev. **35,** 236 (1930).
[4] A. Meissner, Zeits. f. Physik **40.** 839 (1927).

INTENSITIES OF VIBRATION-ROTATION BANDS WITH SPECIAL REFERENCE TO THOSE OF HCl

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Abstract

Intensity formula for vibration bands. The intensities of vibration bands depend on certain matrix elements of the electric moment of the molecule. The electric moment of a diatomic molecule is a function of the nuclear separation and must be expanded in a power series about the equilibrium point. Matrix elements are calculated by perturbation methods for the fundamental and first two harmonic bands of the vibration spectrum, and it is found that, to a first approximation, for the n^{th} harmonic it is necessary to consider the $(n+1)^{th}$ power in the series expansion of the electric moment, and higher powers for better approximations. The formulas for the fundamental and first harmonic are given to a second approximation. The matrix elements are also calculated from wave functions due to Morse for a diatomic molecule, and it is shown that there is a negligible difference between the two methods of calculation for small quantum numbers. Formulas are also given for the ratio of the intensity of the first two harmonic bands to that of the fundamental.

Application to HCl. The formulas derived in the first part are applied to the case of HCl which is the only molecule for which the intensities of the vibration bands have been measured with any precision. New data from wave-length measurements of Meyer and Levin are used and the value of the coefficient of the quadratic term in the power series expansion of the electric moment is found. It is found that two values of this coefficient would give the same intensities and no satisfactory way of resolving the ambiguity is available. Numerically it is found that if the electric moment $p=p_e+p_e'\xi+p_e''\xi^2/2$, then $p_e''=0.070\times10^{-18}$ or 4.56×10^{-18} e.s.u.

Introduction

I HAVE recently shown[2] that the ratio of the measured intensities of the fundamental and harmonic bands of HCl in the near infrared can be predicted quantitatively assuming Morse's[3] vibrational wave function analysis and also that the electric moment of the molecule is a linear function of the nuclear separation. Morse's potential function is not as general as a simple power series expansion of the potential function about the equilibrium point and so there has been some question as to what effect the difference between these forms for the potential function would have on the predicted intensities. It is the purpose of the present paper to compare the intensity formulas obtained from both potential functions and also to consider the effect on the intensities of higher terms in the power series expansion of the electric moment. Briefly stated the results are that the intensity formulas derived by the two methods give numerical results which differ by less than the experi-

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[2] J. L. Dunham, Phys. Rev. **34,** 438 (1929).
[3] P. M. Morse, Phys. Rev. **34,** 57 (1929).

mental error of the measurements, and that the inclusion of higher terms in the electric moment is, in general, necessary. The numerical agreement obtained previously does not have a unique interpretation. Either it is an indication that for HCl the coefficient of the quadratic term is very small indeed, or it is due to a cancellation of terms. The first part of the paper will deal with the derivation of the intensity formulas based on the two potential functions and with a comparison of these formulas; the second part will consider their application to the numerical results for HCl.

Part I

The ratio of the intensities of two corresponding lines in different bands has been shown to be[4]

$$\frac{\alpha_{nm}}{\alpha_{jk}} = \frac{\nu_{nm}}{\nu_{jk}}\left(\frac{P_{nm}}{P_{jk}}\right)^2 \tag{1}$$

where α_{nm} is the intensity of the line $n \rightarrow m$ and ν_{nm} is its frequency. P_{nm} is the matrix component of the electric moment associated with the line $n \rightarrow m$ and will hereafter be called the *intensity integral*. It is calculated from the expression

$$P_{nm} = \int p(r) R_n(r) R_m(r) dr \tag{2}$$

where $p(r)$ is the electric moment of the molecule and is a function of r, the nuclear separation, and $R(r)$ is the radial part of the wave function. If we expand $p(r)$ in a power series about the equilibrium point ($r = r_e$) and change to the dimensionless variable $\xi = (r - r_e)/r_e$, we have

$$p(\xi) = p_e + p_e'\xi + \frac{p_e''}{2}\xi^2 + \frac{p_e'''}{6}\xi^3 + \cdots \tag{3}$$

where $p_e' = (dp/d\xi)_{\xi=0}$ etc., and, correspondingly

$$P_{nm} = p_e'\xi_{nm} + \frac{p_e''}{2}\xi^2{}_{nm} + \frac{p_e'''}{6}\xi^3{}_{nm} + \cdots \tag{4}$$

where $\xi^i{}_{nm} = \int \xi^i R_n R_m r_e d\xi$, is the $(n\ m)^{\text{th}}$ component[5] of the matrix ξ^i.

The expansion of the potential function about the equilibrium point can be written as

$$U = \frac{h\omega_e}{2\theta^2}(\xi^2 + a_1\xi^3 + a_2\xi^4 + a_3\xi^5 + \cdots) \tag{5}$$

where ω_e is the frequency of a classical oscillation for very small amplitudes, $\theta^2 = h/4\pi^2\omega_e I_e \ll 1$, I_e is the moment of inertia of the molecule, and a_1, a_2 and a_3 are arbitrary constants which can be determined from the frequencies of the

[4] This formula was given in reference 2, p. 448. The material for its derivation is given very concisely by E. C. Kemble, Phys. Rev. **25**, 1 (1925); where the only change to be made by the new quantum mechanics is that on p. 6. $\overline{M}^2$ is to be replaced by $P_{nm}{}^2$.

[5] This expansion of P_{nm} is not to be confused with the expansion of charge distribution into dipoles and multipoles. This entire analysis concerns only the dipole radiation.

lines.[6,7] The first term gives the potential of a simple harmonic oscillator, for which the wave functions are known, but the wave functions of the more general case must be calculated by perturbation methods. Fues[7] has calculated the energy levels by this method and has given a formula for evaluating all of the integrals required in the perturbation calculation so that the details of the analysis will not be reproduced here. Suffice it to say that the perturbed wave functions are calculated by straight forward application of perturbation methods and from them the intensity integrals are obtained by Eq. (4).

The intensity integrals for the fundamental and the first two harmonic bands are found to be

$$P_{01} = \frac{p_e'\theta}{(2)^{1/2}}\left[1 + \theta^2\left(\frac{11}{16}a_1^2 - \frac{3}{4}a_2 - \frac{5\rho'' a_1}{4}\right)\right] \tag{6}$$

$$P_{02} = \frac{p_e'\theta^2}{2(2)^{1/2}}\left[(a_1 + \rho'') + \theta^2\left(\frac{243}{32}a_1^3 - \frac{111}{8}a_1a_2 + 5a_3 + \rho''\left(\frac{3}{32}a_1^2 - \frac{15}{8}a_2\right) - \frac{3a_1\rho'''}{2}\right)\right] \tag{7}$$

$$P_{03} = \frac{p_e'\theta^3(3)^{1/2}}{4}\left[\frac{3a_1^2 + 4a_2}{8} + a_1\rho'' + \frac{\rho'''}{3}\right] \tag{8}$$

where $\rho'' = p_e''/p_e'$ and $\rho''' = p_e'''/p_e'$. The formulas for P_{01} and P_{02} have been carried out to a second approximation, and the formula for P_{03} has been given to show how higher derivatives of p enter into the intensity integrals for higher harmonics. There are no reliable intensity measurements for any second harmonic bands so far as I am aware, and consequently P_{03} has been given only to a first approximation.

Mensing and Dennison[8] have obtained by perturbation methods similar to those used here a formula for the intensity ratio of the harmonic to the fundamental band based on the first terms of Eqs. (6) and (7) but omitting the term in ρ'', and Fues[9] has given formulas for the intensity integrals to a first approximation, using Kratzer's potential function, which are closely related to the first terms in Eqs. (6), (7) and (8), but omitting ρ'' and ρ'''. However, the fact that ρ'' enters into the first term of P_{02} in Eq. (7), and that both ρ''' and ρ'' enter into P_{03}, shows that in general these terms cannot be neglected even to a first approximation. Generalizing from the above equations it seems that for the band $(0 \rightarrow n)$ it is necessary to consider at least the first n terms in Eq. (4).[10]

[6] E. C. Kemble, Journ. Opt. Soc. Am. **12,** 1 (1926).

[7] E. Fues, Ann. d. Physik. **80,** 367 (1926).

[8] Note by D. M. Dennison at the end of a paper by Meyer and Levin, Phys. Rev. **34,** 44 (1929). L. Mensing, Zeits. f. Physik **36,** 814 (1926).

[9] E. Fues, Ann. d. Physik **81,** 281 (1926).

[10] The reason for this can be seen quite simply by considering the case of P_{02} in the following fashion. The wave functions are those of an harmonic oscillator made slightly asymmetrical by the anharmonicity of the potential function. The integrand of ξ_{02} is composed of

It turns out that because the expressions for P_{nm} are even or odd in θ, it is necessary to carry the perturbation process two steps farther for each new term in θ added to P_{nm}, a behavior very like that found by Fues for the energy levels.

The frequency ratios which are necessary to calculate the intensity ratios (see Eq. (1)) are given by $\nu_{02}/\nu_{01} \leqq 2(1-x)$ and $\nu_{03}/\nu_{01} \leqq 3$ and the formula for x (which is the coefficient of the quadratic term in the vibrational energy level formula) as given by Fues[7] or Kemble[6] is $x = 3h[5a_1^2/4 - a_2]/16\pi^2\omega_e I_e$ so that the intensity ratios are given by

$$\frac{\alpha_{02}}{\alpha_{01}} = \frac{\theta^2}{2}\Bigg[(a_1+\rho'')^2 + \theta^2\Bigg(\frac{103}{8}a_1^4 - \frac{51}{2}a_1^2a_2 + 10a_1a_3 + \rho''\Big(\frac{53}{4}a_1^3 - 27a_1a_2 + 10a_3\Big) + \rho''^2\Big(\frac{23}{8}a_1^2 - \frac{3a_2}{2}\Big) + \frac{5a_1\rho''^3}{2} - 3a_1^2\rho''' - 3a_1\rho''\rho'''\Bigg)\Bigg] \tag{9}$$

$$\frac{\alpha_{03}}{\alpha_{01}} = \frac{9}{8}\theta^4\Bigg[\frac{3a_1^2+4a_2}{8} + a_1\rho'' + \frac{\rho'''}{3}\Bigg]^2. \tag{10}$$

The derivation of the formulas for P_{01}, P_{02} and P_{03} using the wave functions derived by Morse[3] is similar to the calculation of P_{02} given in reference 2, with the exception that the terms in ρ'' and ρ''' require evaluation of integrals of the type $\int e^{-kx}x^{k-i-1}(\log x)^n dx$. This offers no difficulty as they can be obtained by $(n-1)$-fold differentiation with respect to i of the formula for the integral with $n=1$. Since we are using only small quantum numbers and since $k = 1/x \gg 1$ it is possible to expand the logarithms and radicals appearing in the expressions for P_{nm}[11] in terms of $1/k = x$. This simplifies these expressions considerably.

$$P_{01} = \frac{p_e'(x)^{1/2}}{ar_e}\Bigg[1 + x\Big(\frac{1}{2} + \frac{5\rho''}{2ar_e}\Big)\Bigg] \tag{11}$$

$$P_{02} = \frac{p_e' x}{ar_e(2)^{1/2}}\Bigg[\Big(1 - \frac{\rho''}{ar_e}\Big) + x\Big(\frac{3}{2} + \frac{2\rho''}{ar_e} - \frac{3\rho'''}{a^2r_e^2}\Big)\Bigg] \tag{12}$$

$$P_{03} = \frac{p_e' x^{3/2}}{ar_e}\Big(\frac{2}{3}\Big)^{1/2}\Bigg[1 - \frac{3\rho''}{2ar_e} + \frac{\rho'''}{2a^2r_e^2}\Bigg]. \tag{13}$$

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the product of two wave functions both of which are nearly even functions, and of ξ which is an odd function, so that the *integrand* as a whole is nearly odd. Consequently in the *integral* there is nearly complete cancellation, it being saved from vanishing only by the slight asymmetry of the wave functions. Now ξ is a first order small quantity to begin with, because for low quantum numbers the wave functions are appreciable only for a small range of ξ about $\xi = 0$, so ξ_{02} is a second order small quantity. On the other hand the integrand of ξ_{02}^2 is nearly even, all three factors being nearly even, so that there is no cancellation, but, since ξ^2 is a second order small quantity, the value of ξ_{02}^2 is of the second order too, and therefore of the same order of magnitude as ξ_{02}.

[11] Unfortunately in reference 2, Eq. (13) was incorrectly printed. The factor $A_0A_2k^{k-3}$ should be replaced by $[(k-2)(k-5)/2a^2]^{1/2}$.

From these the intensity ratios can be calculated at once.

$$\frac{\alpha_{02}}{\alpha_{01}} = x\left[\left(1-\frac{\rho''}{ar_e}\right)^2 + x\left(1+\frac{4\rho''^2}{a^2r_e^2}-\frac{5\rho''^3}{a^3r_e^3}-\frac{6\rho'''}{a^2r_e^2}+\frac{6\rho''\rho'''}{a^3r_e^3}\right)\right] \tag{14}$$

$$\frac{\alpha_{03}}{\alpha_{01}} = 2x^2\left[1-\frac{3\rho''}{2ar_e}+\frac{\rho'''}{2a^2r_e^2}\right]. \tag{15}$$

We are now in a position to compare the intensity ratio formulas given by the perturbation method with those given by Morse. This is best done by expanding Morse's potential function in powers of ξ about $\xi=0$ giving

$$U = Da^2r_e^2\left(\xi^2 - ar_e\xi^3 + \frac{7}{12}a^2r_e^2\xi^4 - \frac{1}{4}a^3r_e^3\xi^5\right). \tag{16}$$

There are only two assignable constants in this expression, D and a, whereas in Eq. (5) all the terms have arbitrary coefficients. That is to say there are certain relations connecting the coefficients of all the higher terms in Morse's potential with that of the first term. Now if we impose these relations on the coefficients a_1, a_2 and a_3 in Eqs. (9) and (10), we find that we get exactly Eqs. (14) and (15), so that any numerical differences in the values of intensities calculated by these two methods would be entirely due to slight differences between the potential functions assumed and not to any difference in the mathematical analysis. It has been pointed out by Fues[7,8] that since the harmonic oscillator has no continuous spectrum and since the perturbing terms in the energy go to infinity for large values of ξ, intensity calculations based on this perturbation procedure are not to be relied upon. The identity of the two analyses shown here, however, proves that for low quantum numbers and to the approximations used, the absence of a continuous spectrum in the perturbation analysis has no effect upon the intensities.

A word should be said about the relative accuracy of the two methods. Although for accurate calculations the perturbation method is more precise than Morse's, because the potential function assumed can be fitted to any given molecule more accurately, nevertheless, for first approximations Morse's formulas are to be preferred. The reason is that the first term in Eq. (9) takes into account only the first perturbing term in the potential function, whereas the first term in Eq. (14) contains contributions from higher terms in the potential function as well. In other words Morse's intensity formula converges the more rapidly of the two, so that its *first term* is a better approximation than that of the perturbation formula.[12] For HCl, the numerical difference between the two second approximations is considerably less than the experimental error of the observed intensities. For gases like CO and NO where x is materially smaller than for HCl, the difference is very small even for the first order terms.

[12] Of course perturbation methods could be applied to Morse's wave functions to obtain a more accurate intensity formula, but there is no need of this here in view of the relatively large experimental error.

Part II

We are now ready to turn to a consideration of the numerical values for HCl. Unfortunately there are no accurate data on the intensities of vibration-rotation bands for any other diatomic molecule, as data from imperfectly resolved bands observed with only one tube length or only one pressure are not in the least reliable for intensity measurements.

I have measured the intensity of several lines in the harmonic band of HCl[2] and shown that the observed ratio of the intensity of that band to the intensity of the fundamental band as observed by Bourgin[13] is 0.0161. The probable error of this ratio depends on the probable error of the measured intensities of both bands. The probable error of the harmonic is given (reference 2, p. 445) as 6 percent and Bourgin gives 25 percent as the "precision limits" of his measurements. Interpreting "precision limits" as a figure which the true error is unlikely to exceed, or that there is, say, but one chance in ten of the true error being greater than 25 percent, the probable error for the fundamental turns out to be 10 percent.[14] The probable error of the ratio is given by the square-root of the sum of the squares of the separate errors,[14] which is 12 percent. Thus we have for the observed value of the intensity ratio

$$\frac{\alpha_{02}}{\alpha_{01}} = 0.0161 \pm 0.0019. \tag{17}$$

Dennison,[9] on the basis of observations of Meyer and Levin, has estimated the ratio of these intensities as 0.021 ± 0.004, which agrees, within the limits of error, with the value just given. Dennison's estimate, however, is based on the measurements of one or at most two tube-lengths and so cannot be considered to be as accurate as the value given in Eq. (17).

To compare this value with the theoretical expressions for intensity it is necessary to substitute in Eqs. (9) or (14) the values of the measurable constants of HCl. Meyer and Levin[9] have recently published the results of new measurements of the wave-lengths of the HCl bands under higher dispersion than had previously been obtained and Colby[15] has derived the values of the various molecular constants from their data. These values differ appreciably from the constants used in reference 2. They are:[16]

$$I_e = 2.613 \times 10^{-40} \text{ gm cm}^2 \qquad a = 1.710$$
$$\omega_e = 2988.7 \text{ cm}^{-1} \qquad a_1 = -2.34$$
$$x = 0.01725 \qquad a_2 = 3.62$$
$$r_e = 1.276 \times 10^{-8} \text{ cm} \qquad a_3 = -2.60$$
$$\theta^2 = 0.00709$$

[13] D. C. Bourgin, Phys. Rev. **29**, 794 (1927).

[14] R. T. Birge, Phys. Rev. Supp. **1**, 1 (1929), esp. p. 4.

[15] W. F. Colby, Phys. Rev. **34**, 53 (1929).

[16] The values given are obtained by averaging the results for the two isotope components which is sufficiently accurate for our purposes. The value of a_3 has been obtained by using the value of $a^3 r_e^3/4$ (i.e. the value of a_3 according to Morse's analysis, cf. Eq. (16)). a_3 is a small term occurring only in a second order correction so that a more precise evaluation is not necessary.

Substituting these values in Eqs. (9) and (14) we have:

$$\frac{\alpha_{02}}{\alpha_{01}} = (0.0194 - 0.0166\rho'' + 0.00355\rho''^2) \quad \text{(Pert)} \tag{18}$$
$$(-0.0015 + 0.0008\rho'' + 0.00026\rho''^2 - 0.000147\rho''^3 - 0.000414\rho''' + 0.000177\rho'''\rho'')$$

$$\frac{\alpha_{02}}{\alpha_{01}} = (0.0173 - 0.0159\rho'' + 0.00364\rho''^2) \quad \text{(Morse)} \tag{19}$$
$$(+0.0003 + \quad + 0.00025\rho''^2 - 0.000143\rho''^3 - 0.000376\rho''' + 0.000173\rho'''\rho'')$$

In Eqs. (18) and (19) the two terms in θ appearing in Eqs. (9) and (14) have been kept separate to show that the formula from Morse's analysis converges more rapidly than the other so that its first term may be considered a better approximation than that of Eq. (9). If the two terms are combined, it is easy to see that the difference between the two second approximations cannot be greater than 2 percent, as none of the major terms differ by more than that amount.

In these equations the only unknowns are ρ'' and ρ'''. Unfortunately we cannot evaluate both of these constants from one equation, as the method of successive approximations would not yield very significant results for ρ''' in view of the relatively large experimental error. Consequently we shall use only the first terms and solve only for ρ''. Now, as we have seen, if we are going to use only the first term, Eq. (19) is more accurate than Eq. (18) so that we shall use the former in calculating ρ'', which gives us:

$$\rho'' = \begin{matrix} 0.066 \pm 0.13 \\ 4.30 \pm 0.13 \end{matrix} \tag{20}$$

there being two values because the first term of Eq. (19) is quadratic in ρ''. Now $p'' = p_e''/p_e'$ and, for a known value of p_e' determines p_e''. Using the value of p_e' found by Bourgin[13] ($p_e' = 1.06 \times 10^{-18}$ e.s.u.) we have for p_e''

$$p_e'' = \left.\begin{matrix} 0.070 \times 10^{-18} \\ 4.56 \times 10^{-18} \end{matrix}\right\} \text{e.s.u.} \tag{21}$$

p_e'' is the coefficient of the quadratic term in the expansion of $p(\xi)$ about $\xi = 0$ and consequently is a measure of the "curvature" of the electric moment at that point.

The fact that one of the values of p_e'' is zero (within experimental error) shows why in my previous paper on this subject[2] a calculation of the intensity ratio assuming a linear electric moment gave results in good agreement with the observed value. This correspondence, however, cannot be used to show that p_e'' is negligible because we have just seen that a value of p_e'' which is a good sized positive quantity (a negative quantity if p_e' is negative) *also* gives

the correct value for the intensity ratio, and there is no way, using only intensity data, to distinguish between these two values of p_e''.

A similar ambiguity arises in the case of p_e' where, because of the quadratic dependence of the intensity on the electric moment, it is not possible to determine the sign of p_e' from intensity measurements alone. This ambiguity in the sign of p_e' leads to a sort of double ambiguity in p_e'' because a change of sign of p_e' changes the sign of p_e'' as determined from Eq. (20). This, of course, does not affect that value of p_e'' which is practically zero, but the other greater value may apparently have either sign depending on that of p_e'.

It has always been assumed that the electric moment of HCl is linear and that p_e' is positive in the region about the equilibrium point. These were natural assumptions when HCl was supposed to dissociate into ions, but in recent years, it has been shown that HCl probably dissociates adiabatically into neutral atoms,[17] which means that at least for large values of r, the electric moment decreases with increasing nuclear separation. This surely means that the curvature of the electric moment is appreciable somewhere, and there is no reason why it should be negligible at the equilibrium point, so that we cannot rule out the larger value of p_e'' until there is more detailed information on the form of p as a function of r. As far as the sign of p_e' is concerned, it is probably positive. The position of the hydrogen nucleus when at equilibrium, is generally considered to be inside the M shell of the chlorine atom and so we may assume that its distorting influence on the chlorine atom, and consequently the electric moment of the molecule, is not at its greatest, and hence p is still increasing with r.[18] This is a very rough sort of reasoning but owing to our complete ignorance about the detailed processes responsible for setting up electric moments in molecules with atomic binding, it is the only sort of reasoning that we can apply to the data at present.

[17] V. Kondratjew, Zeits. f. Physik **48,** 583 (1928); R. Samuel, Zeits. f. Physik **49,** 95 (1928); F. London, Zeits. f. Physik **46,** 455 (1928) esp. p. 472 et seq.; Franck und Kuhn, Zeits. f. Physik **43,** 164 (1927) esp. p. 169.

[18] Assuming that the electric moment at r_e is near its maximum and has a positive slope, the most probable value of p_e'' is the small one (nearly zero) because the other implies a large positive curvature which is impossible in the neighborhood of a maximum. However the assump ion that r_e is near the maximum is too questionable to warrant definite predictions and the whole matter may be complicated by subsidiary maxima in the electric moment for values of r less than r_{max}.

THE RAMAN EFFECT IN HCl GAS

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(Received April 23, 1930)

Abstract

Improvements in the experimental conditions made it possible to get much better pictures of the Raman effect of HCl-gas than before. The results are in perfect agreement with what is predicted by the dispersion theory.

THE first report of the Raman effect in the case of a gas at atmospheric pressure was published by R. W. Wood in Nature, February 2, 1929, where it was shown that hydrochloric acid gas contained in a long glass tube mounted in contact with a Cooper-Hewitt glass mercury arc, the whole surrounded by a reflecting cylinder of highly polished sheet aluminum, gave a Raman line excited by the Hg 4046 line, the frequency difference corresponding to an infrared line in the position of the "missing line" of the absorption band at 3μ. In the following number of Nature, Rasetti announced the discovery of the Raman lines of CO and CO_2 also at atmospheric pressure.

The experiments in HCl were more fully described in the Phil. Mag. for April 1929 and it was shown that the 4358 Hg line was accompanied by a series of close companions, corresponding to rotations of the HCl molecule, and it was further shown that the infrared frequencies corresponding to these lines were of very nearly the same wave-length as the *alternate* lines observed by Czerny. An interpretation of these results was given by several investigators independently.[2] Rasetti[1] studied with great success the Raman effect of other diatomic gases at atmospheric or higher pressures.

With the same tube, and with a platinum diaphragm as was employed in the earlier experiment, but with a recently constructed spectrograph equipped with two interchangeable camera lenses, one a large Steinheil portrait objective (F2.5) and the other a Cooke objective of one meter focus, some superior spectrograms of the Raman effect in HCl have been obtained.

A better alignment of the tube was secured and greater precautions taken to exclude all parasitic light. Six, or possibly seven rotation bands appeared on the long wave-length side of Hg 4355 and three (anti-Stokes) on the other side. Rotation bands also appeared on both sides of the 4046 line, but the "Q branch" line excited by 3650–3655 and 3663 appeared in triplicate mixed in with these rotation bands.

[1] F. Rasetti, Nature **123,** 205, 757 (1929). Proc. Nat. Acad. Sci. **15,** 234, 515, (1929). Phys. Rev. **34,** 367 (1929).

[2] G. H. Dieke, Nature **123,** (1929). F. Rasetti reference 1. E. L. Hill and E. C. Kemble, Proc. Nat. Acad. Sci. **15,** 387 (1929), and others. All these papers are simply an interpretation of the formulas of the dispersion theory developed first by Kramers and Heisenberg in 1925.

An enlargement of the entire spectrum is reproduced in Fig. 1. and a highly enlarged portion of the part showing the Q branch excited by 4046 and the rotation bands to the right and left of the 4358 line in Fig. 2.

Fig. 1. Enlargement of entire spectrum.

Fig. 2. Highly enlarged portion of spectrum.

Interpretation of the Results

The Raman effect of HCl furnishes an excellent opportunity to compare the theoretical predictions with the experimental results, for the HCl molecule is very simple, and furthermore we know its entire infrared absorption spectrum. The situation is therefore much more favorable than for the organic molecules, the exact structure of which is generally not known, so that it is impossible to say what we ought to expect theoretically.

The experimental data are given in Table I.

Table I.

λ	$\Delta\nu$	Transition	$\Delta\nu$ infrared
—	—	0→2	62.69
4377.60	101.1	1→3	104.29
85.6	142.7	2→4	146.03
94.2	187.5	3→5	187.45
4402.4	229.4	4→6	228.87
10.4	271.0	5→7	270.03
18.6	312.9	6→8	311.23
26.5	353.0	7→9	352.23
4314.7	143.8	4→2	146.03
23.8	183.3	5→3	187.45
31.2	232.2	6→4	228.87
4581.8	2886.0	j→j	2885.4*

* This line is excited by λ4047. The corresponding line excited by λ4358 would fall in a region where the plate is very insensitive. The infrared datum is the zero line of the absorption band at 3.4μ. The wave-length of the Raman Q-branch has been taken from the previous work because the dispersion was then greater. We find now a value about 3 cm^{-1} less, but think it less reliable.

The first column gives the observed wave-lengths of the Raman lines. The second column gives the frequency differences with the exciting line λ4358.

In the third column we find the rotational transitions in the molecule to which the lines correspond, and the fourth column gives a comparison with the infrared data (see farther down).

The dispersion theory of Kramers and Heisenberg[3] published in 1925 contains, as is well known now, a complete theory of the Raman effect. The more rigid radiation theory of Dirac leads essentially to the same formulae. The essential feature of this theory is, that the intensity of a Raman line which corresponds with a transition of the molecule from the level a to the level b, has no connection at all with the transition probability between these two levels, which would determine the intensity of the corresponding absorption line. In order to find the intensity of a Raman line we must consider virtual transitions with a certain third level c. If this level c can be reached in an ordinary transition from both the levels a and b, the Raman line is allowed. The Raman line can therefore be considered as the difference between two lines of the molecule, one of which must be an absorption line. The theory gives further the exact intensities of the lines expressed in terms of the transition probabilities between the different levels of the molecule, but we need not go here into details of the theory.

If we consider now a HCl molecule in its normal electronic and vibrational state and with a value j of the rotational quantum number, we have to consider first the possible absorption transitions in order to find which Raman lines we have to expect. In any transition the change of j can be only zero or ± 1. From the theory of the spectra of diatomic molecules it is well known[4] that those states to which the molecule can go if $\Delta j = 0$ are of a different nature from those for which $\Delta j = \pm 1$.

Let us consider the latter ones first. The molecule would be either in a state with $j+1$ or with $j-1$ after the virtual absorption act. It has to fall back in a virtual emission act to the *normal* electronic level, and the change of j can only be ± 1 in this transition. After the emission of the Raman line the molecule can therefore only be in a state with the rotational quantum number j or $j \pm 2$. If we take into account also those virtual absorption acts for which $\Delta j = 0$, (such transitions would occur when the upper electronic state is a II-state), nothing will be changed in this result. For in the virtual reemission act j must remain likewise unchanged, so that in this particular kind of Raman transition no change of j can occur. As we have to take the sum over all possible third levels c, our result is that in any Raman transition j can change only zero or ± 2. As for any infrared absorption line of HCl we must have $\Delta j = \pm 1$, we see that not a single Raman line can correspond to an absorption line.

As was shown by Van Vleck[5] the possible changes of the vibrational quantum number are zero or ± 1 only, even if intermediate levels c with high

[3] H. A. Kramers and W. Heisenberg Zeits. f. Physik **31**, 681 (1925).

[4] E. Hulthén, Zeits. f. Physik **46**, 349 (1927). R. de L. Kronig Zeits. f. Physik **46**, 814 (1928).

[5] J. H. Van Vleck, Proc. Nat. Acad. Sci. **15**, 754 (1930).

values of the vibrational quantum number are taken into account. A higher electronic level of the HCl molecule than the normal one is as yet unknown. From the behavior of similar molecules we have reason to expect that an absorption act will result in such a case into dissociation. There seems to be no reason why these dissociated states cannot act in just the same way as the discrete levels as intermediate states in the Raman effect. The considerations which determine the selection rule for j hold just as well for this kind of transition. It may be expected that the probability for the ultraviolet absorption is much greater than that for the infrared absorption so that the transitions via the dissociated states play the most important part in the Raman effect of HCl. But other factors ought also to be considered, so that this point cannot be settled yet with the present material.

If the vibrational quantum number does not change, we can notice only a change ± 2 of the rotational quantum number for $\Delta j=0$ gives the unmodified line. If j *increases* two units we have what is called the normal Raman

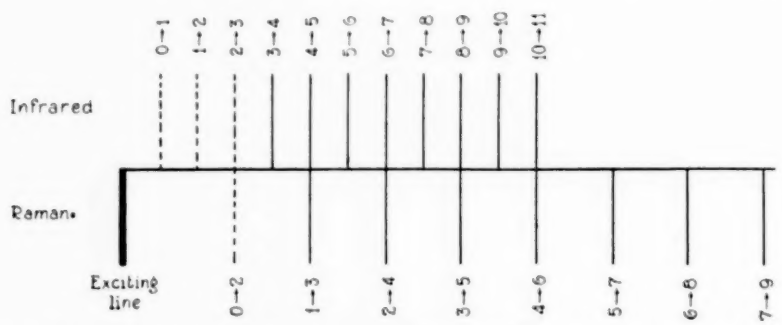

Fig. 3. Diagram showing the connection between the Raman and the infrared rotational spectrum of HCl.

effect,[6] i.e., lines on the red side of the directly scattered line and as the table shows, the transitions up to $7\rightarrow 9$ have been observed except the first one which would come too close to the strong unmodified line so that it cannot be detected. We can obtain the same rotational differences also from the infrared data of the vibrational rotational bands nl. as differences $R(j-1)-P(j+1)$ of lines of the R- and P-branch, and these differences are given in the fourth column of the table.[7] The agreement is as good as it can be expected from measurements of such faint lines.

In the former communication and in the beginning of this paper it was mentioned that these lines correspond with alternate lines of the rotational absorption band in the far infrared observed by Czerny.[8] But this correspondence is only accidental as can be seen immediately from Fig. 3 in which

[6] A sequence for which in the Raman effect $j\rightarrow j+2$ is called an O-branch. It would be similar to an ordinary P-branch with double spacing. Similarly a sequence of lines for which $j\rightarrow j-2$ is called an S-branch.

[7] Taken from C. F. Meyer and A. A. Levin, Phys. Rev. **34,** 44 (1929).

[8] M. Czerny Zeits. f. Physik **34,** 227 (1925); **44,** 235 (1927).

both the Raman and the far infrared absorption spectrum of Czerny are plotted and the corresponding transitions indicated. The fact that the Raman lines coincide with alternate infrared lines is only due to the fact that the rotational energy can be represented with good approximation by $Bj(j+1)$, from which follows that the Raman lines due to the transitions $j+1\rightarrow j-1$ coincide with the absorption lines $2j+1\rightarrow 2j$. This agreement is not exact as one would find deviations if one takes into account also the higher terms in the rotational energy. These deviations are however too small to be noticeable with the accuracy of the present observations.

The conditions for the observation of the Raman lines corresponding to transitions $j\rightarrow j-2$ (anti-Stokes lines, *S*-branch) were much less favorable, as the first lines are covered by the companions of λ4358. However, the three lines given in the table can clearly be recognized. Obviously the distance of a line $j\rightarrow j-2$ from the unmodified line must be the same as that for the line $j-2\rightarrow j$. The intensity of the $j\rightarrow j-2$ transition seems to be less than that of the $j\rightarrow j+2$ transition. This asymmetry can also be accounted for theoretically. For a $\Sigma\rightarrow\Sigma$ transition the probability for a transition $j+1\rightarrow j$ is equal to that for $j\rightarrow j+1$ and proportional to $j+1/2$. For a Raman transition the intensity is determined by expressions in which the product of the probabilities for the virtual absorption and emission act occur. Therefore for a transition $j\rightarrow j-2$ the intensity would be proportional to $(j-1/2)(j-3/2)$ whereas for the transition $j\rightarrow j+2$ the intensity would be proportional to $(j+1/2)(j+3/2)$. That means that a line of the *O*-branch must be stronger than the line of the *R*-branch which has the same initial state, and that is in agreement with the observed intensities.

If the vibrational quantum number increases one unit, we have to expect transitions $j\rightarrow j+2$ (*O*-branch) $j\rightarrow j-2$ (*P*-branch) and $j\rightarrow j$ (*Q*-branch). The *O* and *P* branches were too weak to be noticeable on the plates, which indicates that a Raman transition in which the vibrational quantum number increases one unit is *much* less probable than the transition in which it remains unchanged in accordance with Van Vleck's calculations. All the lines of the *Q*-branch fall so close together that they cannot be separated and are seen as one somewhat diffuse line. As the moment of inertia is larger in the final state of the Raman transition (on account of the stronger vibration) the *Q*-branch ought to be degraded towards the exciting line, i.e. towards the violet. It can clearly be seen on the plate that this is actually the case.

THE PHOTOELECTRIC AND THERMIONIC PROPERTIES OF PLATINUM COATED GLASS FILAMENTS

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Abstract

The photoelectric and thermionic properties of platinum sputtered glass filaments are discussed, special attention being given to the effect of temperature, and to electrolysis of potassium through the glass to or from the sputtered coating. When electrolysis is away from the surface, the photoelectric threshold is independent of the temperature up to 450° and is close to 2720A. With electrolysis toward the surface the threshold remains at 2720A up to 260°C above which it shifts toward the red with rising temperature, reaching a maximum value of about 4300A at 410°C. Electrolysis produces identical effects on the photoelectric and thermionic emissivity for electrons; the effect on positive ion emission is similar, also, except that a peculiar maximum in the emissivity occurs for a specific electrolysis potential. Ultraviolet radiation has no effect on the thermionic emission of electrons or positive ions from this type of filament.

IN A recent article from this Laboratory by F. G. Cottrell, C. H. Kunsman and R. A. Nelson[1] a new method was presented for the production and control of positive ions. The present paper is a continuation of this study, and deals with the photoelectric and low temperature thermionic phases of the problem.

Apparatus

The type of emitter chosen for this research consisted of a platinum filament over which a thin layer of potassium glass* was fused, the diameter being about 1.5 mm. A reserve supply of potassium was provided by immersing the filament in molten potassium nitrate and electrolyzing potassium through the glass onto the filament; the potassium formed a golden brown layer over the filament surface. The emitting surface was a thin layer of platinum deposited on the glass by cathode sputtering; short distances at the ends were kept free to insulate the platinum coating from the filament. Electrical contact to the platinum coating was made by twisting a fine platinum wire tightly around the filament. With this type of filament, potassium could be electrolyzed to or from the platinum coating as desired by placing a suitable potential (V_E) between the coating and the filament.

A schematic drawing of the apparatus is shown in Fig. 1. The temperature of the filament was given by a thermocouple twisted about the coating. The emission currents were read with a Compton electrometer shunted with a

* A donation of the Corning Glass Works.

[1] Cottrell, Kunsman and Nelson, J. O. S. A. **20,** 152 (1930), and in press.

high resistance leak and potentiometer, which enabled currents to be read from 10^{-15} to 10^{-10} amps. The collecting electrode was made of copper, while the filament supports were made of nickel or tungsten. Ultraviolet light was admitted through a 1 inch quartz window with a graded glass seal.

A Hilger monochromatic illuminator was used to resolve the light of a hot mercury arc of the Uviarc type operating at 75 volts and 1.85 amps. The intensities of the various lines were measured with a Hilger thermopile, using the same slit width as that used in the photoelectric measurements, namely 0.5 mm.

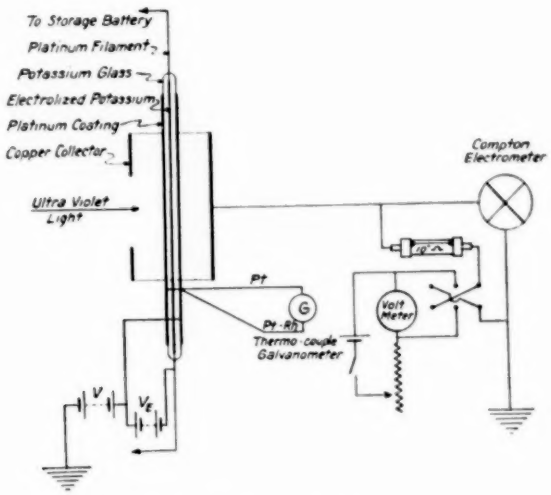

Fig. 1. Diagram of apparatus.

The nature of the filament did not permit of a systematic outgassing process. The pressure in all cases, however, was below the sticking point of mercury in the McLeod gauge (10^{-6} mm of Hg).

Results

Photoelectric emissivity. In determining the photoelectric threshold the current per unit of light intensity method was used. Corning glass filters and direct radiation from the arc were used also where greater intensity was needed.

The factors investigated in this research were (1) the effect of the electrolysis potential between the coating and the filament on the threshold, and on the emissivity; (2) the effect of temperature on the threshold, and on the rate of electrolysis; (3) the effect of electrolysis on the characteristics of the wave-length—current intensity curve, and (4) the effect of ultraviolet light on the thermionic emissivity of both electrons and positive ions.

The effect of an electrolysis potential (V_E) on the photoelectric activity is shown by line *A* of Figure 2.

It will be noted that the emissivity for λ 2653 is changed by an order of 30 fold, when V_E is changed from 1.5 v. negative to 3.0 v. positive. These

voltages, however, are not corrected for the fall of potential along the filament which for this temperature was about 3.0 v., the filament drop being negative to the coating. The zero, therefore, should be moved 1.5 v. to the right in Fig. 2, to give the correct electrolysis potential.

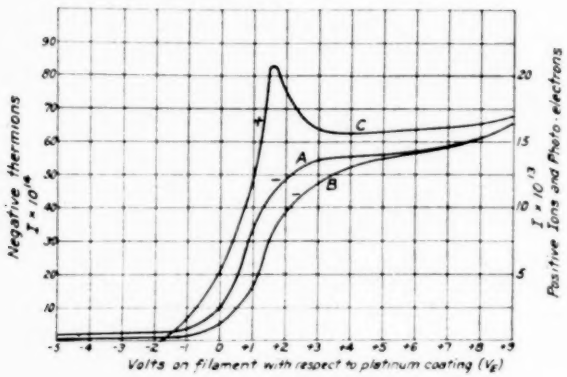

Fig. 2. A. Photoelectric emission, λ2653, temp. 337°C; B. Thermionic emission of electrons, temp. 632°C; C. Thermionic emission of positive ions, temp. 422°C.

In these experiments a constant difference of potential of 45 volts was maintained between the coating and the collector. Saturation was obtained at slightly less than 2 volts and showed no change up to 135 volts.

The effect of temperature on the rate of electrolysis is shown in Figure 3.

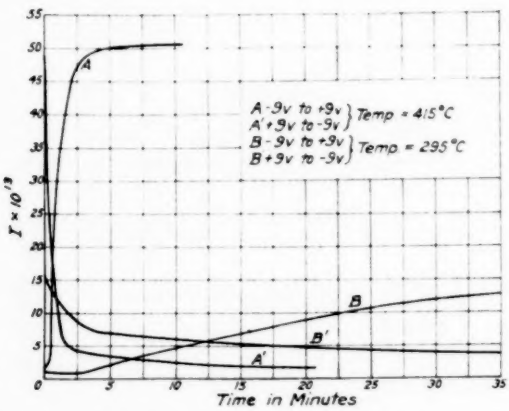

Fig. 3. Effect of temperature on the rate of electrolysis.

It will be noted that at 295°C one hour is required for a steady state to be reached when the electrolysis potential is changed from 9 v. positive to 9 v. negative, or vice versa. At 415°C steady conditions are reached in about 4 minutes, while at higher temperatures the change is too rapid to be measured. At 260° no effect could be observed from changing the electrolysis potential, as is illustrated by line *C* of Figure 4.

A lag exists between the time when V_E is made positive and when an increase in photoelectric activity is observable, the duration of the lag decreasing with rising temperature. On the other hand, the emissivity falls off rapidly the instant a negative electrolyzing potential is applied.

The effects of temperature and electrolysis potential on the threshold and on the specific activity for various wave-lengths are illustrated in Fig. 4.

Line *C*, as has just been stated, represents the current per unit intensity at 260°C for $V_E = +9$ v. and $V_E = -9$ v. This is the lowest temperature at which an electrolysis effect could be observed. These results were obtained with a fresh filament. After the filament had been worked in at temperatures up to 400°C the threshold shifted to a position represented by line *D*.

The long wave-length limit for a worked-in filament with $V_E = -9$ volts was very close to 2720 A, as is shown by line *D*. After the filament was

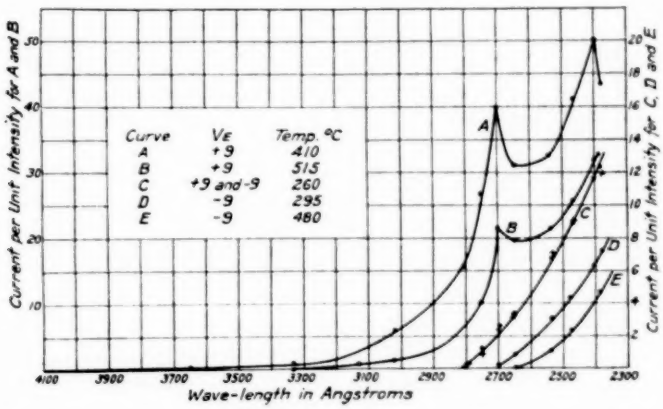

Fig. 4. Effects of temperature and electrolysis potential on the threshold and on the specific activity for various wave-lengths.

once worked in, the temperature coefficient became zero for all temperatures up to 425°C. At temperatures above 425°C the threshold shifted downward as is shown by line *E*, the shift increasing with the temperature.

The electrolysis of potassium to the surface (V_E positive) at temperatures above 260°C results in an enhanced photoelectric activity increasing with V_E as is shown by line *A* of Fig. 2, and with temperature, as is shown by comparing lines *A* and *B* of Fig. 3. The increase in emissivity is accompanied by a nearly corresponding shift in the threshold toward the red.

The conditions for maximum threshold are shown by line *A* of Fig. 4, in which case it was just possible to detect a photoelectric current with λ4350A. As the temperature was raised above 260°C, the threshold moved from about 3130A to 4350A, at 425°C. The exact value depended on the previous treatment of the filament, being higher when the filament had been cooled down with a strong positive electrolyzing potential applied. At temperatures above 425°C the threshold again shifted toward shorter wave-lengths, and the shape of the line became more regular as is shown by

line *B* of Fig. 4. At visibility the threshold shifted to about 3050A. The shift in the neighborhood of redness is due to the combined effect of temperature and fatigue, for the total emissivity cannot be restored by lowering the temperature.

The specific photoelectric activity is apparently abnormally high in the region around 2700A and 2400A as is shown by the breaks in curves *A* and *B*. These irregularities are more pronounced for fresh filaments and when electrolysis to the surface has just been increased by raising the temperature or by increasing the electrolysis potential.

The long wave-length limits, as determined above, were checked with Corning filters using the direct radiation from the arc. At 280° the photoelectric current was about 10^{-10} amp. when the light direct from the arc was passed through 12 mm of Pyrex, which should cut out λ3022A, and fell to 1.1×10^{-13} amps. for a 3.5 mm Noviol O filter, and to about 10^{-15} for 7 mm, which should exclude most of λ3650A; the threshold is, therefore, very close to 3600A. When the temperature was raised to 310°, the photoelectric current increased 4-fold.

The effect of fatigue is especially noticeable at high temperatures; the total activity can be reduced to a third of its initial value by holding the filament at redness for a period of minutes. The activities can usually be restored by reversing the sign of V_E and electrolyzing potassium ions away from the coating. Filaments have also been restored by washing in water and alcohol, and then lightly annealing with a small blue flame.

The thermionic emission of electrons. The thermionic emission of electrons from a fresh surface was detectable at temperatures above 425°C for positive electrolyzing potentials. The effect of V_E on the current is shown by line *B* of Fig. 2. The fall of potential along the filament is not corrected for in the graph; making this correction would shift the entire line 2 volts to the left.

The work function curves obeyed the Richardson equation fairly well, yielding a value for *b* of about 4×10^4. No significance can be applied to this value, however, since the character of the surface definitely changed with temperature.

Special tests were made to detect an enhancement of the thermionic emission in the presence of ultraviolet light. These tests were carried out by balancing out the photoelectric current with the leak potentiometer, while the thermionic current was observed, and then by balancing out the thermionic current and measuring the photo-electric emissivity. Both general and monochromatic radiation were used. No effect of the ultraviolet light could be observed either in the temperature at which thermionic emission became detectable or in the magnitude of the thermionic currents.

The thermionic emission of positive ions. The emission of positive ions became detectable at 270°C. This is very close to the temperature where the photoelectric measurements showed the electrolysis potential to become operative.

The effect of V_E on the positive ion emission at 422°C is shown by line *C* in Fig. 2. The fall of potential along the filament is such that the entire

line should be shifted 1.5 volts to the left, bringing the peak of the curve at approximately $V_E = 0$.

Curve *C* is distinctly different from curves *A* and *B* in that it shows a critical value of V_E at which the maximum ion current is obtained.

The positive ion currents between 270°C and 450°C agree very well with those reported by Cottrell, Kunsman and Nelson, except that the value of ϕ computed from the Richardson equation is higher by about 0.5 volts. The high work function at the low temperature is to be expected from the fact that the rate of electrolysis also increases with temperature, thus increasing the available supply of possible ions at the surface.

A test for the photoelectric emission of positive ions was made, using direct radiation from the arc in which light of wave-lengths below the threshold of the copper collector was screened out by Corex A Blue Purple filters. No photoelectric emission of positive ions could be detected.

Discussion of Results

The fact that the emission of electrons thermally and by ultraviolet light are both affected by electrolysis to and from the surface becomes doubly interesting when the characteristics of curves *A* and *B* of Fig. 2 are considered. By making the necessary corrections for zero potential, it will be seen that the two curves are identical in form and position. This is a further proof for the contention that the same group of electrons in the metal contribute to photoelectric and thermionic emission,[2] and is in line with the results of DuBridge[3] and of Warner[4] who have shown that the work functions for the two types of emission are identical.

Line *C* for positive ion emission is also very similar to lines *A* and *B* for electron emission, except for the fact that it contains an optimum value of V_E. It will be noted that the photoelectric activity increases rapidly at the value of V_E where positive ion emission becomes detectable.

The similarity between the positive ion and electron curves as well as the presence of an optimum electrolysis voltage for positive ions is readily explained by applying to the Richardson equation the intrinsic force concept previously outlined by the writer.[5, 6, 7]

In the equation $i = ne(kT/2\pi M)^{1/2}e^{-b/T}$, n is the number of possible positive ions per unit volume at the surface of the emitter, while b is a measure of the work done in bringing such an ion through the surface region. From this it follows that any process which decreases n or raises b will decrease the positive ion current.

The electrolysis of positive ions away from the surface ($-V_E$) decreases the value of n; line *C* of Fig. 2 shows that the positive ion emission is not de-

[2] Sommerfeld, Zeits. f. Physik **47,** 1 (1928).
[3] DuBridge, Phys. Rev. **31,** 236 (1928).
[4] Warner, Proc. Nat. Acad. Sci. **13,** 56 (1927).
[5] Brewer, Proc. Nat. Acad. Sci. **12,** 560 (1926).
[6] Brewer, Proc. Nat. Acad. Sci. **13,** 592 (1927).
[7] Brewer, J. Phys. Chem. **32,** 1006 (1928).

tectable for large negative values of V_E. The increase in the positive ion current as shown on the graph from $V_E = -1.75$ to $V_E = +1.5$, is without doubt due to an increase in the value of n.

The accumulation of an element of large atomic diameter such as potassium on the surface should, according to the intrinsic force concept, increase the value of b for positive ion emission just as it decreases b for negative emission. The decrease in emissivity beyond the critical value of V_E is due, therefore, to an increase in the thermionic work function for positive ions occasioned by the accumulation of potassium at the surface. Thus the electrolysis of potassium to the surface increases both n and b for positive ion emission, the observed emission curve being a resultant of these two effects.

The fact that an electrolysis potential larger than 3 volts positive has only a small effect on the emissivity, as may be seen from Fig. 2, raises the question as to the nature of the potassium on platinum surface. A condition such as this may result either from the surface being completely covered with potassium at this point, or from a state of polarization being reached in the surface layer which prevents a further accumulation of potassium.

Two facts may be mentioned which indicate that a state of polarization exists and that the surface does not become covered with free potassium. First, in Fig. 3 it will be seen that the emissivity drops markedly the instant a negative electrolyzing potential is applied. Had the surface been covered with a layer of potassium, lines A' and B' should have shown a time lag. The second fact is that it was never possible to obtain the threshold for pure potassium, the values found always lying between that for potassium and platinum. It would seem, therefore, that the surface can best be considered as a surface solution of potassium in platinum rather than a deposit of potassium on platinum.

The writer's best thanks are due Dr. C. H. Kunsman for his interest and advice, and Mr. R. A. Nelson for constructing the filament and rendering other valuable assistance.

THE ROLE OF THE CORE METAL IN OXIDE COATED FILAMENTS

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Abstract

Temperature-power relations have been determined for numbers of oxide coated filaments. Part of these filaments had cores of platinum-10% iridium and others had cores of "Konel," an alloy of nickel, cobalt, iron and titanium. Oxide coated Konel is a much better radiator than oxide coated platinum-iridium which causes a considerable difference in their temperature -input power characteristics. Nevertheless, emission measurements show that oxide coated Konel filaments yield higher electron emissions than oxide coated platinum-iridium under the same conditions of filament power. Experimental proof is also given that these filaments need no activation other than the decomposition of the alkaline earth carbonates to oxides in vacuo. The enormous difference shown between the emission characteristics of these two types of oxide filament necessitates the conclusion that the core metal has a definite function other than simply a mechanical support for the alkaline earth oxides.

Suggested mechanism of thermionic emission from oxide coated filaments. In order to account for this difference, a modification is suggested in existing ideas concerning the mechanism of emission from this type of cathode. This modification consists in assuming that the source of emission is the composite layer formed by occlusion of alkaline earth metal on the surface of the core and that the electrons emitted diffuse through the interstices in the oxide coating into the vacuous space. Argument is presented to show that this explanation will also account for other peculiarities in the behavior of oxide cathodes. (1) The decay of emission during life may be explained by a slow sintering of the coating and a consequent closing of these pores. (2) De-activation of the filament by over-heating may be attributed to the same cause. (3) Non-saturation may be due to a pseudo-space charge formed by occlusion of electrons on the surface of the coating particles.

Introduction

SINCE the discovery by Wehnelt[1] in 1904 of the exceedingly large electron emissions obtainable from glowing calcium oxide, this type of hot cathode has steadily become of greater and greater importance both for use in various thermionic devices and as a copious source of electrons in work of purely scientific interest. This popularity has followed closely upon necessary improvements in technique, resulting in a much greater degree of uniformity from filament to filament as well as in a constant improvement in their efficiency. An inspection of the values of the work function for the alkaline earth oxides obtained by various investigators in the chronological order in which their results were obtained is an excellent proof of this improvement. A table of this sort is appended for which we are indebted to Espe.[2]

[1] Wehnelt. Ann. d. Physik **14,** 425–468 (1904).

[2] Espe, Wissenschaftliche Veroffentlichungen aus dem Siemens Konzern, **5,** 29–46 (1927).

Observer	Material	$d\phi$ (volt)	$d\phi'$ (volt)
Wehnelt 1904	CaO	3.67	
	BaO	3.85	
Horton 1907	CaO	4.11	
Deininger 1908	CaO	3.76	
Jentzsch (1908)	CaO	3.48	
	SrO	3.87	
	BaO	3.58	
Schneider (1912)	CaO	3.45	
Cook and Richardson (1913)	CaO	2.4	
Germerhausen (1916)	CaO	2.54	
Wilson (1917)	CaO	3.28–3.94	
	BaO 50%		
	SrO 50%	2.02–2.16	
	BaO 50%		
	SrO 25%	2.34–2.59	
	CaO 25%		
Arnold (1920)	BaO+SrO	1.67–2.05	
Davisson and Germer (1923)	BaO+SrO	1.79	
Spanner (1924)	CaO	2.4	
	SrO	2.15	
	BaO	1.85	
Koller (1925)	BaO 60%		
	SrO 40%		1.04
Rothe (1926)	(Five Commercial Tubes)	0.64–1.24	
Espe (1926)	CaO	1.93	1.77
	SrO	1.43	1.27
	BaO	1.11	0.99

As a result of the composite nature of this type of cathode the phenomena attendant upon its use are quite complicated and of a somewhat different nature than those found upon examination of pure metallic cathodes. This complexity has given rise to several schools of thought in regard to the mechanics of electron emission from this class of material. It has been held:

1. That the emission is derived from the oxide *per se*,
2. That it is the result of a chemical reaction within the coating, and
3. That the emission comes from a layer of metallic barium on the surface of the oxide coat.

To the best of the author's knowledge the effect of the base or core metal has always been held to be negligible or has been entirely ignored. This is, perhaps, a natural consequence of the various ideas concerning the nature of the oxide emission which have been held up to the present and to the fact that nearly all students of this subject have used platinum as the core metal to the exclusion of everything else. Schottky and Rothe in Vol. 13, chapter IX page 227 of the Wein-Harms Handbuch der Experimental Physik (1928) have summed up the situation very nicely as follows: "Aus einer der ersten Untersuchungen der Oxydemission durch F. Deininger geht hervor, das diese (i.e., the work functions for various oxides) unabhängig von dem Material des Glühdrahtes und eine charakteristische Eigenschaft des betreffenden Oxyds ist, wie es auch allen unseren Anschauungen über die Wirkung von Oberflächenschichten entspricht."

Results which have been obtained in this laboratory indicate that the core metal does play a very important rôle in the behavior of this type of hot cathode and therefore that the explanations stated above are misleading as to the true nature of this emission, or at best, are inadequate. It is the purpose of this paper to set forth proofs that the core metal has a vital function in the phenomena of oxide emission. It is also our purpose to suggest an explanation of the mechanics of emission which will take into account this newly discovered factor as well as conform to the demands of their better known but equally important characteristics.

With the advent of the oxide coated filament into common use in radio receiving tubes, it became an economic necessity to find a satisfactory substitute for platinum-iridium as the core metal. Dr. Dayton Ulrey of this laboratory suggested that nickel was the logical metal to begin with. Experiment showed that quite as good emissions could be obtained from oxide coated nickel filaments as had ever been gotten from the oxide coated platinum filaments then in use. The subsequent almost universal adoption of this material for commercial use has entirely corroborated the results obtained by the author at that time.

The search for a satisfactory platinum substitute was not abandoned with the proof that nickel could be used with equally good results. A metal having a higher tensile strength at red heat and above was desirable to insure longer life before burn out as well as less danger of breakage.

An alloy of nickel, cobalt, iron and titanium was found to meet these requirements and also to give excellent thermionic results when coated with oxides of the alkaline earths in the usual way. This alloy has received some publicity of late under the name "Konel."

During the course of investigation of oxide coated Konel filaments in commercial tubes of the UX-112 type it was noted that the brightness temperature of these filaments appeared to be considerably lower than that of similar oxide coated platinum filaments operating at the same power per unit area. This observation seemed to call for a careful study of the relative operating temperatures of these two types of filaments, since neither theory nor experience could account for the effect noticed. This investigation was carried out in the manner described in the succeeding paragraphs.

Experimental Method and Results

The filaments used during the course of this investigation have all been of the type used in UX-281 Radiotrons. Both the platinum-10% iridium (referred to hereafter in this paper simply as platinum) and the Konel filaments were coated in the same fashion. Several applications of a water paste consisting of equal parts of $BaCO_3$ and $SrCO_3$ were baked on the ribbon in an atmosphere of CO_2. This carbonate coating was subsequently decomposed to oxide in vacuo during the outgassing process of the tube to be examined. Since all data given are averages obtained from a rather large number of filaments made from different spools of ribbon and coated at different times, their exact dimensions are irrelevant. Their approximate dimensions were

27 cm length by 0.06 cm width. Both the platinum and the Konel filaments had practically the same areas and resistance characteristics. This equality of area insures equal space charge limitations when mounted in tubes whose anodes are all of the same size. The filaments were mounted *M* fashion in standard UX-281 tubes save that for the temperature investigation no anodes were included. No corrections for cooling effects of the leads and hooks have been applied since a careful test showed that this effect was negligible when plotting the temperature of the center of the filament against the power input to the filament.

This test was carried out on a tube in which were mounted two filaments as shown in Fig. 1. These filaments were taken from the same spool of coated ribbon but were of different lengths. They were connected in series

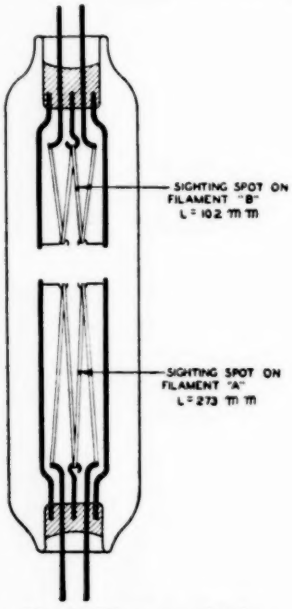

Fig. 1. Diagram of tube.

so that by subtracting the voltage drop through the shorter filament from that through the longer one the power loss in the uniformly heated central portion of the longer filament could be calculated. Further calculation showed that the end cooling on a filament of this length was responsible for an error in the curves of about 3 degrees in the lower range of temperature and about 1 degree in the upper range. The target for optical pyrometer observations on the base metal was formed by carefully scraping the coating from one side of the ribbon at the center of one of the middle legs of each filament for a space about equal to the width of the filament. Brightness temperature observations were made on this spot as well as on the surface of the coating at a point immediately adjacent to this bare area. Two Leeds & Northrup optical pyrometers calibrated against standard lamps furnished by Dr. Forsythe of Nela Park were used for this work, the results of

which are shown in Fig. 2. It may be well to call attention to the fact that each point plotted is an average of five separate observations and each point of a group was found for a different filament. A check test was run recently on two of the filaments previously studied using a different pyrometer. The results of this check are indicated by crosses. It seems entirely safe to conclude from the results shown that the brightness temperature curves given here are not in error by more than $\pm 5°C$.

Obviously, we are interested in the true temperature of the core metal and not particularly in that of the surface of the coating. In order to calculate the true temperature of the Konel filaments it became necessary to find the value of its spectral emissivity at $\lambda = 0.65\mu$ in the temperature region under investigation. This was accomplished by the spiral filament

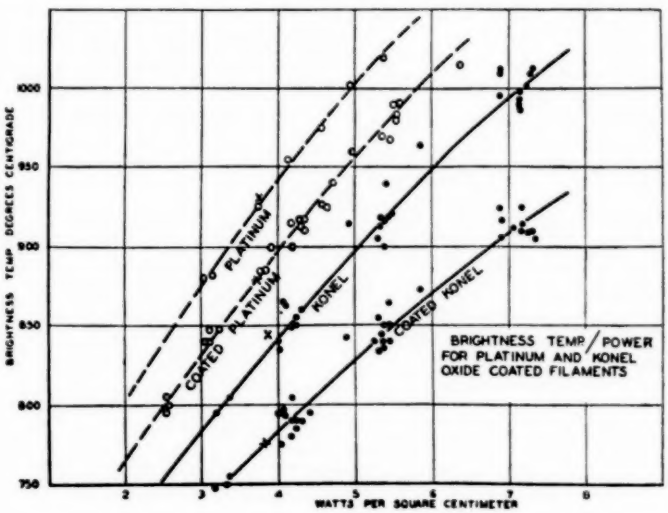

Fig. 2.

method described by Shackelford[3] with the result that a value of 83% was found for this factor. Foote and Fairchild[4] give this correction factor for platinum as 33% and for iridium as 30%. A rough calculation of the spectral emissivity of the coatings yields a value of the order of 25%. This value is of course only approximate since the difference in temperature between the surface of the coating and that of the base metal is not precisely known, although it can at the most be a matter of only 10 to 15 degrees C. Furthermore, these coatings, although appearing pure white by reflected light are quite porous as well as translucent, with the result that the above value is probably high.

By applying the proper correction factors to the curves of Fig. 2 we arrive at the values shown in Fig. 3 which refer of course to the true temperature

[3] Shackelford, Phys. Rev. **8**, 470–478 (1916).

[4] Foote & Fairchild, Symposium on Pyrometry, Am. Inst. Mining & Met. Eng. 338, (1920).

of the metal cores as a function of the power supplied to the filaments in watts per cm^2.

The difference in temperature between oxide coated platinum and Konel filaments operating under like conditions of power input is readily explained. Konel becomes considerably oxidized during the coating process described above and hence is a much better radiator than platinum. The oxide coating, although a poor radiator, allows an appreciable amount of the radiation from the core to escape owing to its porosity and translucence. As a result the energy radiated is dependent upon the nature of the core

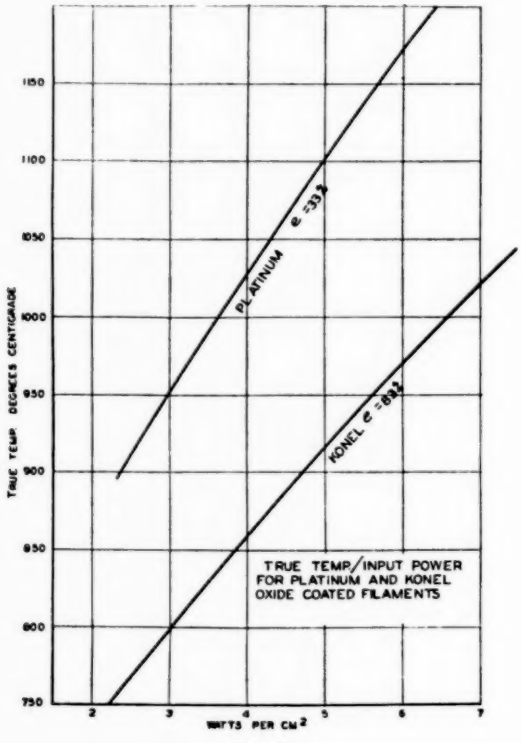

Fig. 3.

to a considerable extent and is not limited entirely by conduction through and radiation from the surface of the coating.

In Fig. 4 are shown some space current measurements made with UX-281 Radiotrons using similar filaments to those used in the tests described above save that these filaments have a length of approximately 17 cm. In fact, some of them were taken from the same spools of coated ribbon. These curves are also averages for numbers of tubes and show that when the currents are limited by emission rather than by space charge the values for oxide coated Konel are higher than for oxide coated platinum operating at the same power per unit area. It must be borne in mind that the results given here are to be considered as typical of this particular kind of coating. It is possible that different results might be obtained with, for example,

the barium azide method of coating. The whole process of making oxide filaments, coating them with oxides and their subsequent treatment on the pumps is of the nature of an art only to be acquired through long practice. The author would, therefore, hesitate to comment on the results to be obtained by some distinctly different process of coating. The filaments used

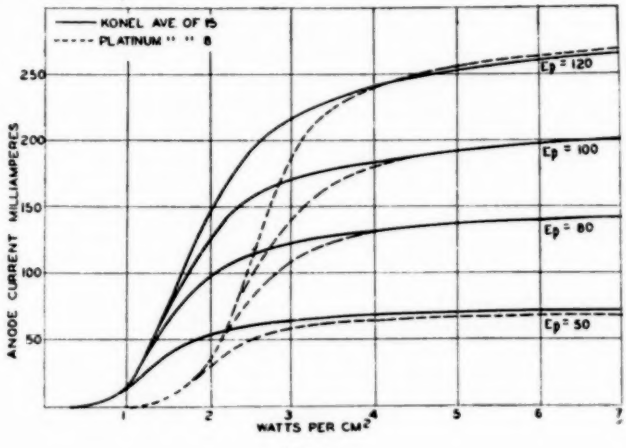

Fig. 4.

throughout this work were good representative samples of commercial oxide coated filament. The tubes used were also representative in every way, their only difference from commercial tubes being that the most extreme care was used in getting the highest obtainable vacuum in each one to obviate the possibility that any appreciable part of the space currents obtained was due

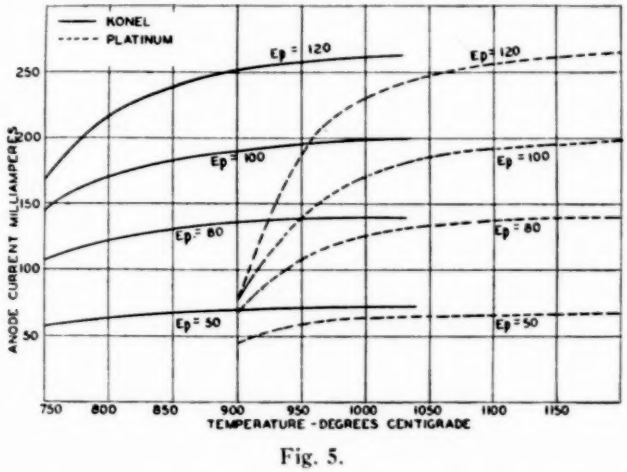

Fig. 5.

to the presence of gas. The normal value of emission for UX-281 Radiotrons is 0.170 amperes at $E_p = 100$ volts and a power input of approximately 4 watts per cm^2.

The results of the previous curves have been combined to obtain the results shown in Fig. 5. Here are shown the space current values obtained

at various anode voltages plotted against the temperature of the filaments in degrees C. It here becomes obvious that the core metal has an enormous effect on the thermionic activity of the coating. It is readily seen from these curves that the same anode current may be obtained from oxide coated Konel at 775°C. as can be obtained from platinum coated with the same oxides at 950°C. This is the phenomenon which we believe is new and for which we offer a possible explanation in the succeeding pages.

The Mechanics of Emission

As mentioned in the introductory matter of this paper, at least three distinctly different explanations of the mechanics of emission from oxide coated filaments have been set forth in the past. None of them take into account any function of the core metal other than as a mechanical support for the thermionically active oxides and as a means of furnishing the necessary thermal energy to them in a convenient manner. The experimental facts stated in the foregoing pages make it imperative that the role of the core metal be recognized and its effect explained. It is obvious that such an explanation must also be in accord with other phenomena peculiar to this type of cathode. Some of these phenomena are:

1. The formation process.
2. Destruction of activity by overheating.
3. Decay of activity with life.
4. Non-saturation.

The explanation most in favor during recent years has been that offered by Koller,[5] Espe,[6] Rothe[7] and others in which it is assumed that the source of activity is a layer of metallic barium on the surface of the oxide coating. Espe argues that this barium is formed by electrolytic decomposition of the oxide coating and that the barium diffuses to the surface of this coating where it serves as emission centers. The explanation submitted herein is a modification of this idea in that it is believed that the emission arises from a layer of metallic barium occluded on the surface of the core metal or alloyed with it. This modification seems necessary in that if the emission arises from the oxide itself or from barium "emission centers" on the surface of the coating, the thermionic activity of such filaments should be unaffected by the nature of the core. In such case both platinum and Konel oxide filaments should be equally active at like temperatures. This obviously is far from the fact.

In a way, it is immaterial to the argument at hand as to just the method by which the barium is produced. If it is formed by electrolytic decomposition according to Espe,[6] the barium ions would be positively charged and have a natural tendency to migrate toward the core. As a matter of fact this is probably the method by which a constant supply of barium on the core is maintained after the initial "activation."

[5] Koller, Phys. Rev. **25,** 671, (1925).
[6] Espe, reference 2.
[7] Rothe, Zeits. f. Physik **36,** 737–758 (1926).

It is also possible that metallic barium is formed by positive ion bombardment under certain conditions of activation. This explanation does not, however, account satisfactorily for a maintenance of a barium supply under high vacuum conditions.

With the type of coating used by the author in the course of this work it is, however, entirely probable that the barium is formed either by thermal decomposition of the carbonates in vacuo or by the reducing action of the metallic core. Figure 6 shows a curve of the behavior of a typical filament during the course of an experiment to prove this point. Tube #X2410 containing Konel filament #125–386 was baked at 400°C in the usual way, after which the metal parts of the tube were thoroughly outgassed in a high

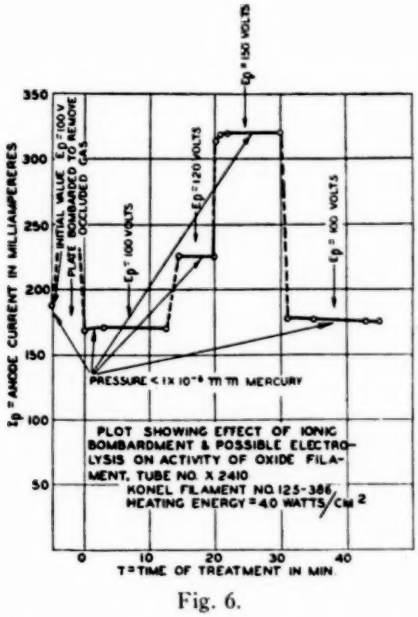

Fig. 6.

frequency furnace. The only heating received by the filament up to this time was that due to radiation from the hot anode. An instantaneous measurement of emission was then made and yielded a value of 5×10^{-6} amp. at a filament power input of 4 watts per cm^2 and an anode voltage of 100 volts. The filament was then heated at 8.5 watts per cm^2 for several minutes and then at 5–6 watts per cm^2 until the gas pressure in the tube had been reduced to less than 1×10^{-5} mm of mercury. During this treating out of the filament no anode voltage was applied and the plate was cold except for radiation absorbed from the filament. Another instantaneous determination of the emission now gave 0.186 amperes under the same test conditions as before. Subsequent treatment of various kinds gave no improvement as is indicated by the curve, which is self explanatory. This behavior is typical of this type of filament when properly handled. Similar results have been obtained with oxide coated platinum filaments, so the results described can-

not be ascribed to the kind of base metal used. Since a certain amount of vaporization of the barium from the core is to be expected at operating temperature especially in the case of platinum filaments, it is quite likely that the supply of barium is replenished by some such process as the electrolytic decomposition of the oxide coating. It certainly is not essential however to their initial activation. Again we must insist that this applies only to coatings of the type used in this work. If the carbonates are converted to oxide by long continued heating in the air and not converted in vacuo as in this case, an activation process of some length does have to be followed to bring the filaments up to normal activity.

Evidence of this and also of the fact that the emission is due to metallic barium was obtained in an experiment similar to the one just described in which the filament was burned in air at low pressure for a short time after it had been tested as above with identical results. The burning in air had the result of enormously reducing its activity (to about 5×10^{-6} amp.) and it was only by heating it for some hours in high vacuum with a constant application of 200 volts on the anode that its activity was restored to the same order of magnitude that it had originally.

A necessary consequence of our hypothesis is that the electrons leaving the emitting layer must diffuse through the interstices in the oxide coating. This consequence presents no serious difficulties. Indeed, it offers a solution to some of the perplexing problems connected with the behavior of this type of cathode. At best, the electrical resistivity of these oxide coatings is very high even at glowing temperatures. In fact, Dr. C. T. Ulrey of the Research Laboratory of the Westinghouse Lamp Company during the course of some yet unpublished work has not been able to obtain a discontinuity in the space current curve for such filaments when the anode was made to approach the filament until it actually touched the surface. Furthermore, these coatings are very porous. When viewed through a microscope they have the appearance of a light fluffy fall of snow. It seems reasonable to suppose therefore that the escaping electrons may diffuse through this oxide layer which, however, does offer some impedance to their progress. Suppose now that this coating should become more compact so that its pores are partially closed. The natural consequence would be that the apparent activity of the filament would be measurably impaired. This is precisely the type of phenomenon that does occur. It is well known that glowing the filament for a comparatively short interval of time at a considerable overvoltage will practically ruin its emission. It has been the author's experience at least that a filament which has been so mistreated cannot, in general, be reactivated to anything like its original characteristics. It is also true that such filaments will, after such reactivation as is possible, yield large emissions if very high anode voltages are applied. The net result of such an overheating of a filament is essentially to increase the impedance of the tube by an appreciable amount. This we believe to be caused by a partial closing of the pores of the coating. Preliminary microscopic examination of some such filaments actually showed a sintering or glazing of the coating until it had the appearance of a crackled enamel.

Exactly similar behavior is shown by filaments whose activity has gradually decreased during a long period of use. Such worn out filaments always retain an appreciable amount of coating. In fact, a fairly close inspection shows that they still possess nearly as thick a layer of oxide as they had initially. In this case also large emissions may be drawn if sufficiently high anode voltages are applied.

If the loss of activity in these cases were due solely to a loss of metallic barium due to vaporization it should be possible to cause these filaments to regain all their initial activity by electrolysis or by positive ion bombardment. As stated above it is rarely if ever that it is possible to do this.

The process of electron diffusion through a porous, poorly conductive coating may also explain the phenomenon of non-saturation which is commonly met with in this type of cathode. It follows logically that large numbers of electrons will become enmeshed in the pores of the coating or occluded on the surface of the particles of poorly conducting material composing it. It is quite possible also that the numbers of electrons so entrapped will vary somewhat with the anode voltage applied. This process will give rise to an effect similar to a negative space charge within the confines of the coating itself. The space currents obtainable then at any given anode voltage and filament temperature represent the number of electrons per second it is possible to drag out of or through this negative charge built up within the coating layer. The result will be that much higher anode voltages will be required to approach a saturation than if this pseudo space charge did not exist. At temperatures in the neighborhood of 1000°C the electron emission from these filaments is so enormous that it is next to impossible to obtain anything approaching saturation owing to the very considerable heating effects of the emission itself. At these temperatures also the conductivity of the coatings will be increased appreciably affording a better opportunity for the electron charge to leak off.

Conclusions

In view of the experimental results presented in the foregoing pages, we are forced to accept the fact that the base or core metal does affect appreciably the electron emission from the alkaline earth oxides. This situation in turn demands a modification of existing ideas concerning the mechanism of emission from oxide cathodes.

An hypothesis is offered concerning this mechanism in which:

1. The source of emission is assumed to be a layer of metallic barium (or other alkaline earth metal) occluded on the surface of the base metal or alloyed with it. In this case the constants of the well-known Richardson equation must be characteristic of the composite surface.

2. The electrons emitted from this composite surface must diffuse through the pores of the coating.

3. The coating in turn, as a function of its porosity, offers considerable impedance to the progress of the electrons.

4. The occlusion of electrons on the particles of the coating sets up a pseudo space charge effect which serves to explain the phenomena of non-saturation as well as the fading of emission during short periods of operation.

5. The gradual decay in activity of coated filaments during life is due to a slow sintering of the coating resulting in a closing of its pores and a consequent increase in the impedance offered to the passage of electrons. A similar process occurs if the filament is strongly glowed for a comparatively short interval of time with or without anode voltage.

It is admitted that no crucial tests of this explanation have been offered with the exception of that showing the pronounced influence of the core metal; which, of course, is the effect which makes the above modification in existing ideas necessary. Numerous experimental investigations are now under way in this laboratory which have been designed as tests of the various assumptions made herein. It is hoped that these tests will be far enough along to permit of their publication in this magazine in the near future.

In conclusion, the author wishes to express his gratitude to Dr. C. T. Ulrey of the Westinghouse Lamp Company Research Dept. and to Drs. D. L. Ulrey and N. Rashevsky of this laboratory for their interest and for the helpful suggestions received from them during the progress of this work.

ON THE THEORY OF THE SOLAR CORONA*

By E. O. Hulburt
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Abstract

The outer atmosphere of the sun is assumed to be composed mainly of ions and electrons which are actuated by gravitation, radiation pressure and the magnetic field of the sun. By distillation along the lines of magnetic force the particles collect in the lower latitudes of the solar outer atmosphere and by their diamagnetism reduce the magnetic field approximately to zero in this region, leaving a stray field at the poles. Thus the polar plumes, prominent during sun-spot minima, are regarded as owing their form to the magnetic field of the sun. Whereas the wide spreading structureless coronal luminosity extending out from the lower latitudes is due to an accumulation of ionization which reduces the magnetic field to a low value and permits the radiation to blow the particles out to great distances. During maximum solar activity there is sufficient ionization of the outer atmosphere to reduce the magnetic field to a low value even at the poles, and hence the outer atmospheric spray extends roughly equally in all directions, in accord with the appearance of the corona.

DURING minimum solar activity the corona spreads out from the sun between latitudes about 50° north and south as shown in Fig. 1.[1] In this region the luminosity is mainly structureless, with of course irregularities such as clouds and prominences. The polar plumes are short and well defined. During maximum solar activity the corona extends more or less equally in all directions, as in Fig. 2,[2] with no marked polar plumes. At times the luminous streams ejected from the active latitudes around 40° give the corona roughly the outline of a square. The material of the corona is considered to be very attenuated, for comets have been observed to pass through it without being damaged.[2] The coronal particles were found, from Doppler effects, to be moving outward from the sun[3] with velocities around 20 km sec^{-1}. In the present paper the assumption is made that the outer atmosphere of the sun is composed of ions and electrons, and it is shown that the particles, due to the influence of gravitation, radiation pressure, and the magnetic field of the sun, form an atmosphere which has approximately the observed shape of the corona.

From measurements of the Zeeman effect of spectrum lines in the chromosphere Hale[4] has shown that the magnetic field of the sun is similar to that of a uniformly magnetized sphere. The magnetic field around a uniformly

* Published with the permission of the Navy Department.

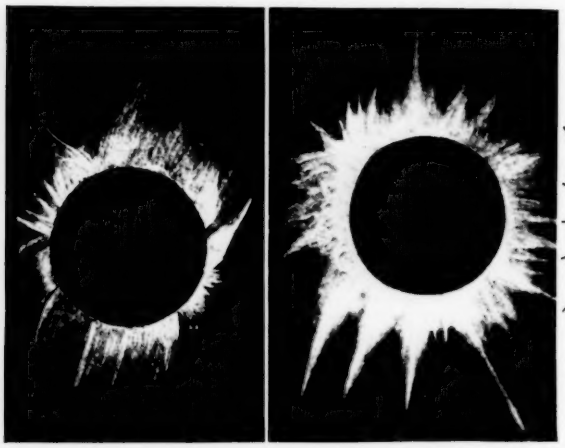
[1] Slocum, Astrophys. J. **64,** 145 (1926).

[2] Mitchell, "Eclipses of the Sun" (1924).

[3] Russell, Dugan and Stewart, "Astronomy" **2,** 509 (1927).

[4] Hale, Astrophys. J. **38,** 31 (1913); Hale, Sears, van Maanen and Ellerman, Astrophys. J. **47,** 1 (1918).

magnetized sphere is drawn in Fig. 3. The magnetic field of the sun was found to decrease along the radius, falling from 55 gauss to less than 10 gauss in a distance of a few hundred kilometers measured radially outward.[4] Gunn[5] explained the radial degradation of the magnetic field by means of the diamagnetism of the long free path ions and electrons in the chromosphere; various drift currents may add to or subtract from the diamagnetic effect but perhaps not to a great extent.



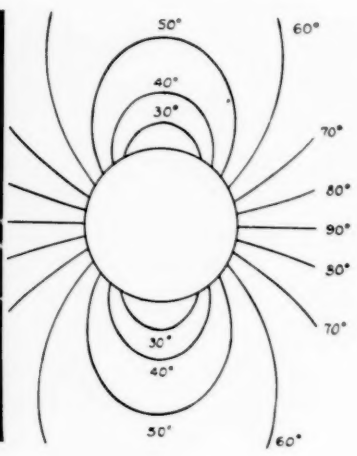


Fig. 1. Fig. 2. Fig. 3.

Fig. 1. Drawing of the eclipse of January 24, 1925, near minimum solar activity.
Fig. 2. Drawing of the eclipse of August 30, 1905, near maximum solar activity.
Fig. 3. Magnetic field of a uniformly magnetized sphere.

If a region contains y long free path ions or electrons per cm^3 and if H is the impressed magnetic field in the region, the ions and electrons by their diamagnetism cause a reduction in H. The condition that H be reduced to a small value is expressed by[5]

$$y \geqq H^2/4\pi kT, \tag{1}$$

where T is the absolute temperature of the ions and k is the Boltzmann constant 1.371×10^{-16} erg deg^{-1}. Although accurate enough for the present discussion (1) is an approximation, for it neglects the possible warping of the field H by the diamagnetic cloud.

In order for diamagnetism to exist we must have

$$\gamma \geqq \rho, \tag{2}$$

where γ is the free path of the ion and ρ is the radius of gyration of the ion about H. Assuming that all the particles are ions of mass m, diameter $\sigma = 3\times10^{-8}$ cm and velocity v,

$$\rho = mv/He, \tag{3}$$

[5] Gunn, Phys. Rev. **33**, 614 (1929), **35**, 635 (1930).

and

$$\gamma = 1/(2)^{1/2}\pi y\sigma^2. \tag{4}$$

From (1) with T of order 10^4 °K and with H of order 10^{-3}, 10^{-4} and 10^{-5} gauss at various regions of the corona y can not be greater than 10^6, 10^4 and 10^2, respectively. From (2) it follows that the ions can not reduce the field to zero, for if H is very small ρ from (3) is so large that (2) is not satisfied. For example, with m of order 10^{-23} grams and v of order 10^5 cm sec^{-1} H can not be reduced by the diamagnetism of the ions to less than 10^{-7}, 10^{-9} and 10^{-11} gauss for $y = 10^6$. 10^4 and 10^2, respectively. However, this slight remnant of the magnetic field is of no interest here, for it does not influence the motion of the coronal ions appreciably.

It is assumed that the outer regions of the chromosphere are composed mainly of ions and electrons, each cm^3 containing approximately an equal number of positively and negatively charged particles, and that the particles are forced outward by radiation pressure with velocities around 20 km sec^{-1}. A mechanism of radiation pressure has been discussed by Milne[6] and need not be described here. The diamagnetism of the ions reduces the solar magnetic field to small values in the outer chromosphere. Let us suppose that the magnetic field outside of the chromosphere were that of a uniformly magnetized sphere, as Fig. 3, with a value of, say, 1 gauss at chromospheric levels at the equator. The positive and negative ions and electrons, forced out by radiation pressure, follow along the lines of magnetic force in tight spirals; with $m = 10^{-23}$ grams, $v = 2\times 10^6$ cm sec^{-1} and $H = 1$ gauss ρ from (3) is 12.6 meters, which is very small compared to distances in the corona. In general, wherever the magnetic field is more or less normal to the radiation pressure the ions accumulate sufficiently to break down the field. Thus the charged particles ejected between the latitudes 50° north and south are constrained to move in the space between the 50° magnetic line, Fig. 3, and the sun. They accumulate in this space until by their diamagnetic action they reduce the magnetic field to very small value, practically to zero. From (1) with T of order 10^4 °K and $H = 1$ gauss y is 10^{11}. Therefore, when y reaches 10^{11} the guiding action of H is destroyed. The ions thereupon steam out from the sun in the lower latitudes to form a structureless luminosity similar to that of Fig. 1.

In polar latitudes the lines of magnetic force are nearly parallel to the force of radiation pressure. The ions slide out along the lines of force without hindrance and large ion densities in the polar regions of the corona are not built up. Therefore the corona in the polar zones does not extend to such great distances from the sun as it does in the lower latitudes. The polar magnetic field is not destroyed; it guides and is outlined by the flying ions. Thus the short polar coronal plumes are formed, as are observed during solar quiescence, Fig. 1. During maximum solar activity we may suppose that sufficient numbers of ions are ejected to wipe out the magnetic field in the coronal regions at all latitudes, thereby permitting the coronal ions to move out more or less uniformly in all directions, as in Fig. 2.

[6] Milne, Monthly Notices, Roy Ast. Soc. **87**, 697 (1926–27).

The solar latitudes around 40° are the regions of greatest activity, the eruptions being in general more frequent there than in other areas of the solar surface. It is possible that enough ions may be emitted to reduce H to zero above the 40° line, Fig. 3, and yet because of a less rapid supply of ions in latitudes below 40°, H may be appreciable in the lower latitudes within the coronal regions bounded by the 40° line. Thus the present view is not incompatible with Deslandres' hypothesis[7] that H is of the order 10^{-7} gauss. The hypothesis was advanced to explain the curvature of certain solar protuberances, on the idea that the material of the eruption carried an excess charge, either positive or negative, and therefore in its progress across the magnetic field would move in a curved path. The hypothesis may, however, not be necessary, for in certain cases, at least, asymmetrical radiation pressure, as suggested by Pike,[8] may cause the curvature of the prominences. The curious twining and curvature occasionally observed in the long coronal streamers and filaments may be evidence of remnants of the distorted magnetic field.

The total brightness of the corona is about 10^{-6} of that of the sun, and the luminosity falls off roughly with the inverse fourth to sixth power of the distance from the center of the sun[2]. The ions and electrons of the coronal atmosphere are pushed out from the chromosphere by radiation pressure, the pressure acting mainly on the ions which, by their electrostatic attraction, drag the electrons along with them. The ions absorb the sunlight, thereby being subjected to radiation pressure, and reemit a portion of the absorbed energy as coronal light. The radiation pressure acceleration[9] p is given by

$$p = I\beta/mc, \tag{5}$$

where I is the energy flux of the sunlight which is absorbed by the ion with ionic absorption coefficient β, m is the mass of the ion and c is the velocity of light. If a fraction f of the absorbed energy is reemitted as coronal radiation I_c, then

$$I_c = f\beta I y_c, \tag{6}$$

where y_c is the total number of ions in the corona.

The total energy flux in all wave-lengths from the solar surface is 6.2×10^{10} erg cm^{-2} sec^{-1}. Assuming that 10^{-3} of this, corresponding to the energy in the ultraviolet region from about 1500 to 1800A, is absorbed by ions of mass $m=10^{-23}$ grams and absorption coefficient $\beta=5\times10^{-16}$, I is 6.2×10^{7} and p from (5) is 10^{5} cm sec^{-2}. This is somewhat greater than the solar gravitational attraction acceleration 2.75×10^{4} cm sec^{-2}, which is as it should be if the coronal ions are forced out from the sun by radiation pressure. If the ion density y is 10^{6} ions cm^{-3} in the outer chromosphere and falls off with the inverse fifth power of the distance from the center of the sun, y_c is about 10^{40} ions. With these values and with $f=10^{-5}$ in (6) I_c is 3×10^{27} erg sec^{-1}. The total

[7] Deslandres, Comptes Rendus **189**, 413 (1929).
[8] Pike, Monthly Notices, Roy. Ast. Soc. **88**, 3 (1927).
[9] Cf. Hulburt, Phys. Rev. **35**, 1098 (1930), section 8.

radiation I_s emitted by the sun amounts to 3.7×10^{33} erg sec^{-1}. Thus the coronal energy I_c is 10^{-6} of I_s in accord with observation.

Equations (5) and (6) are valid no matter what processes of light absorption and emission are assumed, i. e. whether the processes are those of fluorescence, Raman radiation, resonance scattering,[10] etc. On the other hand, Anderson's[11] very startling theory of the corona makes quite a different set of hypotheses and therefore uses equations different from (5) and (6). The theory assumes that positive electricity is continually annihilated in the sun leaving the sun negatively charged, that the excess negative electrons are driven out mainly by electrostatic forces to form a pure electron atmosphere around the sun and that the coronal light is the solar radiation scattered from this atmosphere. As far as can be seen the considerations advanced in the foregoing paragraphs in explanation of the geometrical form of the corona will hold equally well on Anderson's theory as on a radiation pressure theory. Probably a final decision about the constitution of the coronal atmosphere can not be reached as long as the origin of the lines in the spectrum of the corona remains unknown.

In conclusion the present paper can hardly be regarded as offering a quantitative theory of the corona. It presents a few quantitative ideas about the processes which may be important in the corona and thus furnishes a framework on which to build a quantitative theory. To work out the ideas in more exact detail promises to be a difficult problem, entirely apart from the fact that the development will have to deal as best it can with many unknown quantities and uncertainties of assumption.

[10] Unsöld, Zeits. f. Physik. **46,** 765 (1928).
[11] Anderson, Zeits. f. Physik **42,** 475 (1927), **41,** 51 (1927).

DISTRIBUTION OF NON-REACTING FLUIDS IN THE GRAVITATIONAL FIELD

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Abstract

The paper consists essentially of an analysis of the equations given by Lewis and Randall for the distribution of non-reacting ideal fluids in a gravitational field. When the fluids are incompressible a formal solution is obtained, for a mixture of any number of constituents. But it has not been possible to put it into a form convenient for numerical application. The ratios of the concentrations of any constituent at the top to that at the bottom of a vertical column of the mixture are given explicitly, both for incompressible and compressible fluids. When all the molar volumes of the various fluids are equal the equations are solved completely and lead to a *relative* barometric distribution, and in the particular case of ideal gases, to individual barometric distributions. The physical meaning of this is briefly discussed. The case of binary mixtures is treated in detail, and numerical examples are given, first for a mixture of two paraffins, and secondly for a dilute solution of NaCl in water which is equivalent to an ideal solution of liquids. As is to be expected, the effect is extremely small, and in the first case only one tenth as large as is given by a simple barometric formula.

I. Introduction

ALTHOUGH we might predict, *a priori*, that the effect of gravity in causing a variation with height in the composition of a mixture of non-reacting fluids is but a slight one, it is of interest to have explicit theoretical expressions for this effect. As yet, this has not been attained in the general case of a mixture of any number of constituents: however, the problem of a binary mixture of two ideal fluids has been completely solved and some results of interest have been obtained for the general case. These results and the general problem will be discussed in the following.

Gouy and Chaperon[1] first, and later Duhem[2] and van der Waals[3] considered binary mixtures thermodynamically, but they do not present explicit formulae for the results. Even earlier, however, Gibbs[4] derived the general conditions of equilibrium for a mixture of any number of fluids, but he applied them only to the ideal gas mixture. The conditions of Gibbs are:

(a) The temperature, T, be uniform throughout the mixture;

(b) $$\mu_i + gz = \text{constant} \tag{1}$$

where μ_i is the intrinsic potential of the i^{th} constituent, and z is the height above a fixed horizontal plane.

(c) $$dp = -g\rho dz \tag{2}$$

[1] Gouy and Chaperon, Ann. Chimie Physique **12**, 384 (1887).
[2] Duhem, Jour. de Physique **7**, (1888).
[3] van der Waals, Die Continuität des Gasförmingen und Flüssigen Zustandes, II, p. 30.
[4] Gibbs, Thermodynamics, p. 146 and p. 159.

where $p = p(z)$ is the pressure at z, and $\rho = \rho(z)$ is the density of the mixture at z.

II. The Differential Equations for the Effect

The general differential equations for the effect were then set up by Lewis and Randall.[5] Their method is the following:

Considering any constituent separately, the i^{th} for example, the second law of thermodynamics requires that under equilibrium conditions throughout the mixture

$$dF_i = \frac{\partial F_i}{\partial z}dz + \frac{\partial F_i}{\partial p}dp + \frac{\partial F_i}{\partial \bar{n}_i}d\bar{n}_i + \sum j \frac{\partial F_i}{\partial \bar{n}_j}d\bar{n}_j = 0, \tag{3}$$

where $F_i = F_i(p, z, T, \bar{n}_i, \bar{n}_j)$ is the partial molal free energy of this constituent and $\bar{n}_i = \bar{n}_i(z)$ is its mol fraction. This is obviously equivalent to Gibb's condition (1).

Clearly, if w_i is the i^{th} molar mass,

$$\frac{\partial F_i}{\partial z} = w_i g, \tag{4}$$

and by the second law of thermodynamics,

$$\frac{\partial F_i}{\partial p} = \overline{V}_i \tag{5}$$

where $\overline{V}_i = \overline{V}_i(p)$ is the partial molal volume for the i^{th} constituent.

Now for ideal solutions, to which the present considerations will be restricted, $\overline{V}_i$ is by definition equal to the i^{th} molar volume, V_i, at the pressure p and temperature T. This is a consequence of the criterion that an ideal solution must obey the law of additivity of volumes. Also, in this case,

$$\frac{\partial F_i}{\partial \bar{n}_j} = 0, \; j \neq i \qquad \frac{\partial F_i}{\partial \bar{n}_i} = \frac{RT}{\bar{n}_i} \tag{6}$$

where R is the gas constant, per mol. Combining (2), (4), (5) and (6) with (3):

$$\frac{d\bar{n}_i}{dz} = \frac{\bar{n}_i g}{RT}[\rho v_i - w_i] \quad i = 1, 2, \cdots r \tag{7}$$

if there are r constituents. This is the final form given by Lewis and Randall.

To get the explicit solution to the problem under consideration, the system of simultaneous equations (7) must be integrated, since the composition is essentially given by the $\bar{n}_i$. In principle, (7) would be immediately integrable in the case of incompressible fluids, except for the term $\rho = \rho(z)$ which must be determined from the equations together with the $\bar{n}_i$. This difficulty is not serious in itself, since $\rho(z)$ may be expressed in terms of the $\bar{n}_i$, and in this way eliminated; for, by definition,

$$\rho = \sum_i w_j n_j \tag{8}$$

[5] Lewis and Randall, Thermodynamics, p. 242.

where n_j is the number of mols of the j^{th} constituent per cc of mixture. Also, the definition of the ideal mixtures implies that

$$\sum_j v_j n_j = 1. \tag{9}$$

Hence

$$\rho = \frac{\sum_j w_j n_j}{\sum_j v_j n_j} = \frac{\sum_j w_j \bar{n}_j}{\sum_j v_j \bar{n}_j}. \tag{10}$$

Alternatively, (10) may be derived from the equations (7) themselves: by adding the equations (7) and noting that by definition

$$\sum_j \bar{n}_j = 1 \tag{11}$$

$$\sum_j \frac{d\bar{n}_j}{dz} = \frac{d}{dz} \sum_j \bar{n}_j = 0 = \frac{g}{RT}\left[\rho \sum_j v_j \bar{n}_j - \sum_j w_j \bar{n}_j\right]$$

which is identical with (10).

Putting (10) into (7), the latter becomes a system of non-linear coupled equations:

$$\frac{d\bar{n}_i}{dz} \sum_j v_j \bar{n}_j = k\bar{n}_i \sum_j \bar{n}_j (v_i w_j - v_j w_i) \tag{12}$$

where $k = g/RT$; $\rho_i = w_i/v_i$.

III. Integration of the Equations

The general system (12) has not been integrated completely, except in the case of a binary mixture. However, when all the v_i are equal, (12) or (7) can be solved exactly for a mixture containing any number of constituents.

Returning to (7), its integral is, clearly:

$$\bar{n}_i = c_i e^{-kw_i z + k\int v_i \rho dz} \tag{13}$$

and hence

$$\frac{\bar{n}_i}{\bar{n}_j} = \frac{n_i}{n_j} = \frac{c_i}{c_j} e^{kz(w_j - w_i) + k\int \rho(v_i - v_j)dz}. \tag{14}$$

However, as $\rho(z)$ is unknown until the $\bar{n}_i$ themselves are known, (13) or (14) do not give the solution to the problem in a form which can be applied to any specific case. If the v_i are taken to be constant, ρ can be eliminated from (12), giving

$$\frac{(\bar{n}_i)^{1/v_i}}{(\bar{n}_j)^{1/v_j}} = \frac{(c_i)^{1/v_i}}{(c_j)^{1/v_j}} e^{kz(\rho_j - \rho_i)}. \tag{15}$$

But, although there is yet the relation (11) to be imposed on the $\bar{n}_i$, the system (15) cannot in general be solved for the $\bar{n}_i$.

On the other hand, for the special case where

$$v_i = v_j = \cdots = v, \text{ for all values of } z, \tag{16}$$

(14) gives

$$\frac{\tilde{n}_i}{\tilde{n}_j} = \frac{n_i}{n_j} = \frac{c_i}{c_j} e^{kz(w_j - w_i)}. \tag{17}$$

This equation clearly implies that

$$\tilde{n}_i = c_i e^{-kzw_i + \phi(z)}, \tag{18}$$

$$n_i = c_i e^{-kzw_i + \psi(z)}. \tag{19}$$

Applying (11) to (18)

$$\tilde{n}_i = \frac{c_i e^{-kzw_i}}{\sum_j c_j e^{-kzw_j}} \tag{20}$$

and applying (9) to (19)

$$n_i = \frac{c_i e^{-kzw_i}}{v \sum_j c_j e^{-kzw_j}}. \tag{21}$$

From (2), (8), and (21) it now follows that

$$\int v dp = RT \log \sum_j c_j e^{-kzw_j}. \tag{22}$$

If v is known as a function of p, (22) will give p, and hence v as a function of z. This, when put into (21), gives n_i explicitly as a function of z. The constants c_i may then be determined, in principle, by applying the conditions that:

$$\int_0^h n_i dz = N_i \tag{23}$$

where z is measured from the bottom of the vessel containing the mixture and h is the height of the free surface above $z=0$; N_i is the total number of mols of the i^{th} constituent in the mixture.

If v is not a function of p, (21) itself gives the final solution to the problem, after the determination of the c_i by (23).

It may seem that (16) is a very strong restriction upon the mixture constituents. Nevertheless, the important case where these constituents are perfect gases satisfies (16). For the molar volume is the same for all perfect gases at a given temperature and pressure, and they obviously form "ideal mixtures." In fact, for perfect gases

$$v_i = v_j = \cdots v = \frac{RT}{p}. \tag{24}$$

When this is put in (22), it gives

$$p = \text{const.} \sum_j c_j e^{-kzw_j}. \tag{25}$$

Thus, by applying again (24), (21) becomes:

$$n_i = n_0 e^{-kzw_i}. \tag{26}$$

This is the ordinary barometric formula derived quite differently by Gibbs, though usually tacitly assumed without explicit justification. Here, it results from a very special case of the general equations.

In addition to the case of perfect gases, (16) would be satisfied by a set of non-reacting liquids whose molar volumes happen to be the same, or nearly the same, since the liqiuds may be taken as incompressible. (21) is the complete solution under these circumstances.

Finally, the fact that we get the barometric formula (17) under the assumption that all the v_i are equal, whereas, when this assumption is not made the distribution law is quite different, is of added interest in that it suggests the physical basis of the effect under consideration. If we mix a number of substances whose molecules interact in no way with each other, it is clear that a barometric distribution of the type given by (17) will result, since before mixing each had a barometric distribution. Hence, variations from barometric distributions must be related to the interactions between the molecules. For the present purposes, we may consider a molecule and its field of force to be characterized by its "effective volume," i.e., the volume per molecule in the ensemble, and we note that the assumption of ideal mixtures means that, on mixing at constant pressure and temperature, these effective volumes are not changed.

If, then, to a homogeneous substance is added another with molecules of the same effective volumes, it is apparent that to the original molecular type the added ones will be indistinguishable, in the matters of collisions and perturbing forces, from molecules of their own kind, and vice versa. The effect will be essentially that of increasing the total number of molecules of either kind. Thus, we should expect the *relative* distribution to be barometric, as it was before mixing. Only for ideal gases will the individual distributions be barometric, but the relative distributions in all such cases will be of the type given by (17).

On the other hand, when the effective volumes of the added molecules are different from that of the original kind, the added molecules will exert different forces upon those originally present from those which the latter exert between themselves. Under these circumstances, we cannot expect even the relative distributions to remain as they were before mixing. Hence, in this general case we may get a distribution quite different from that given by (17). In fact, for the example given below of a binary mixture in which the effective volumes differ by a factor of about 2, we find that the distributions given by (15) and that given by a barometric formula may differ by a factor of 10.

Thus, in this qualitative way we can understand the physical basis for the analytical simplicity involved in the assumption of equal molecular volumes for all the molecular species.

Before discussing in detail the binary liquid mixture, it may be of interest to examine (15) further. If (15) be written as

$$\frac{(\tilde{n}_1)^{1/v_1}}{(\tilde{n}_j)^{1/v_j}} = c_j e^{kz(\rho_j-\rho_1)} \quad c_1 = 1 \tag{15'}$$

and if $s \equiv (\tilde{n}_1)^{1/v_1}$, then

$$\frac{s^{v_j}}{\tilde{n}_j} = c_j^{v_j} e^{kzv_j(\rho_j - \rho_1)}$$

and

$$\tilde{n}_j = 1 - \tilde{n}_1 - \sum_l \tilde{n}_l = 1 - s^{v_1} - \sum_l \frac{s^{v_l}}{c_l^{v_l} e^{kzv_l(\rho_l - \rho_1)}}$$

so that

$$\sum_j \frac{s^{v_j}}{c_j^{v_j} e^{v_j z(\rho_j - \rho_1)k}} = 1 \tag{27}$$

This is an equation for s as a function of z. Provided the c_j were known, it could be readily solved numerically for any value of z. But as the c_j are implicitly determined by (23), it is very difficult to express them directly in terms of the N_i. However, if, in the particular problem under consideration, the object is to study the variation in composition from an assumed composition at a given height, (27) will suffice. As

$$c_j = \frac{[\tilde{n}_1(h)]^{1/v_1}}{[\tilde{n}_j(h)]^{1/v_j}} e^{-kh(\rho_j - \rho_1)}, \tag{28}$$

the composition assumed at the height h, will give the c_j, and (27) will then give the composition at any other height.

Finally, it should be pointed out that, both for incompressible and compressible fluids, the ratio of the concentrations f_i, defined as the mol-fraction, of any constituent at the top to that at the bottom of the vessel containing the mixture, can be found in the general case. Considering first the incompressible fluids, if h be the height of the vessel and M the total mass of the mixture for the volume of unit section of height h, then (13) taken between the limits 0, h, gives

$$\frac{\tilde{n}_i(h)}{\tilde{n}_i(0)} = \frac{f_i(h)}{f_i(0)} = e^{-kw_i h + kv_i M} \equiv A_i. \tag{29}$$

If an average density be defined by $\bar{\rho} = M/h$, then

$$\frac{f_i(h)}{f_i(0)} = A_i = e^{kv_i h(\bar{\rho} - \rho_i)}. \tag{30}$$

Thus, if $\rho_i < \bar{\rho}$, the composition of the i^{th} constituent at the top is greater than that at the bottom and, conversely, if $\rho_i > \bar{\rho}$. This of course, would be expected.

If the fluids are compressible, we may consider their molar volumes, v_i, to be given as a function of the pressure. In this case, applying (2) to (13), we get

$$\tilde{n}_i = c_i e^{-kzw_i - k/g \int v_i(p)\, dp}. \tag{13'}$$

We may consider $\int v_i(p)dp = b_i(p)$ as known. Then, taking (13′) between the limits 0 and h, we get:

$$\frac{\bar{n}_i(h)}{\bar{n}_i(0)} = \frac{f_i(h)}{f_i(0)} = e^{-kw_ih - k/g[b_i(p_0) - b_i(p_0 + Mg)]} p(h) \equiv p_0. \tag{30a}$$

For any particular case, the expressions for $b_i(p)$ may be put into (30a) and the actual ratios of the concentrations may then be determined numerically.

IV. The Binary Mixture

We shall first treat the binary mixtures of incompressible fluids. In this case, (15) does permit of an explicit solution. Letting

$$\left.\begin{aligned} t &= \frac{\bar{n}_1}{\bar{n}_2} = \frac{n_1}{n_2} \\ \bar{n}_1 &= \frac{t}{1+t}; \quad \bar{n}_2 = \frac{1}{1+t} \end{aligned}\right\} \tag{31}$$

then

Hence, by (15)

$$\frac{1}{v_1}\log t + \left(\frac{1}{v_2} - \frac{1}{v_1}\right)\log(1+t) = \text{const} + kz(\rho_2 - \rho_1). \tag{32}$$

Now from (29) and (11)

$$A_1\bar{n}_1(0) + A_2\bar{n}_2(0) = 1$$

which, combined again with (11), gives

$$\left.\begin{aligned} t(0) &= \frac{1 - A_2}{A_1 - 1} \equiv t_0 \\ \bar{n}_1(0) &= \frac{1 - A_2}{A_1 - A_2}; \quad \bar{n}_2(0) = \frac{A_1 - 1}{A_1 - A_2} \end{aligned}\right\} \tag{33}$$

so that

$$\frac{1}{v_1}\log\frac{t}{t_0} + \left(\frac{1}{v_2} - \frac{1}{v_1}\right)\log\frac{1+t}{1+t_0} = kz(\rho_2 - \rho_1). \tag{34}$$

As t_0 is known, (34) gives explicitly the variations of the composition t with z. The density of the mixture is then

$$\rho = \frac{w_1 t + w_2}{v_1 t + v_2}. \tag{35}$$

The actual magnitude of the effect may be more directly inferred from the extreme values of the concentrations $\bar{n}_1(0)$ and $\bar{n}_2(0)$, given by (33) and (29), or by the extreme values of the density. These latter are easily found to be by (35), (33), and (29)

$$\left.\begin{aligned}\rho(0) &= \frac{w_1 - w_2 + w_2A_1 - w_1A_2}{v_1 - v_2 + v_2A_1 - v_1A_2} \\ \rho(h) &= \frac{A_1A_2(w_2 - w_1) + A_1w_1 - A_2w_2}{A_1A_2(v_2 - v_1) + A_1v_1 - A_2v_2}.\end{aligned}\right\} \tag{36}$$

Referring to (23), we let $N_1/N_2 = c$, and noting that $N_1w_1 + N_2w_2 = M$, $N_1v_1 + N_2v_2 = h$, A_1 and A_2 take the values

$$A_1 = e^{kv_1v_2(\rho_2-\rho_1)h/v_1c+v_2};\ A_2 = A_1^{-c}. \tag{37}$$

Thus, $\rho(0)$ and $\rho(h)$ can be expressed directly in terms of c and h. For comparison with these formulae, we may note the expression for the composition which would be given by a barometric distribution. This latter is

$$t^1 = \frac{n_1}{n_2} = \frac{N_1w_1(1 - e^{-kw_2h})}{N_2w_2(1 - e^{-kw_1h})}e^{k(w_2-w_1)z}. \tag{38}$$

We see that here the molar volumes V do not enter at all. Yet, this is in complete agreement with our physical picture of the phenomenon, according to which a barometric distribution implies that all the molar volumes are equal and hence do not explicitly affect the distribution. The fact that c does not enter in the expressions as $t^1(h)/t^1(0)$ is simply a corollary of the same reasoning.

The forms of (36) and (37) indicate that the effects of gravity, which we have been considering, should be entirely beyond experimental observations for any reasonable values of h. The following computation will give an example of the actual magnitude of the effect. We consider a mixture of two members of the paraffin series, heptane and octodecane, mixtures of which are very nearly "ideal." Let the temperature be 293°K. The data are

w_1(heptane) $= 100.12$; $\rho_1 = 0.684$; $v_1 = 146.374$
w_2(octodecane) $= 254.30$; $\rho_2 = 0.777$; $v_2 = 327.284$

Let $c = 1$. The computation gives for

$h = 100$ meters: $\rho(0) = 0.74834$
$\rho(h) = 0.74818$

$h = 1000$ meters: $\rho(0) = 0.74901$
$\rho(h) = 0.74750.$

The composition variation according to (34) is plotted in Fig. 1 and, for comparison, is added the composition curve which would be given by the barometric formula (38).

It is of interest to observe that, for this case at least, the incorrect barometric formula would indicate a rather appreciable variation of composition, whereas the equation (34) gives a quite negligible variation.

As a final example, it may be mentioned that, since a dilute solution is equivalent to an "ideal" mixture, the present formulae may be applied to such a case as a dilute solution of NaCl in water. Thus, if $c=100$, $T=300°\text{K}$.

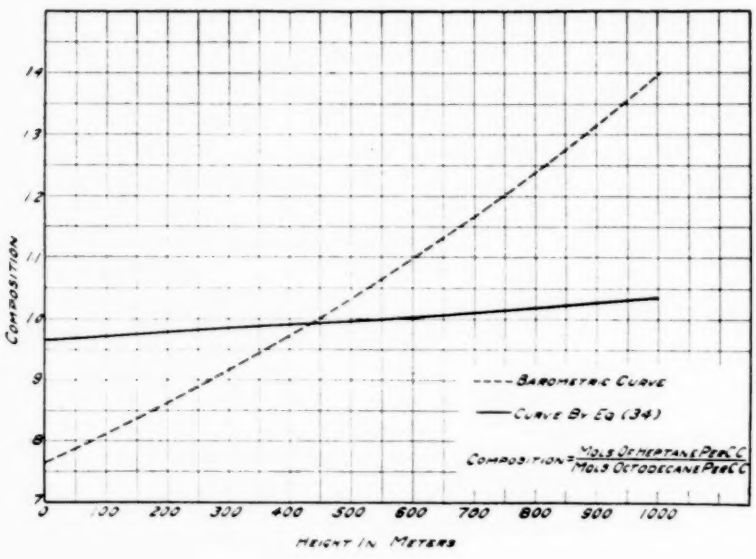

FIG. 1.

$$w_2(\text{NaCl}) = 58.457; \quad \rho_2 = 2.17; \quad v_2 = 26.939$$
$$w_1(\text{H}_2\text{O}) = 18.016; \quad \rho_1 = 1.00; \quad v_1 = 18.016$$

the extreme values for $\rho(0)$ and $\rho(h)$ are, for a depth of 1000 meters,

$$\rho(0) = 1.01809$$
$$\rho(h) = 1.01571$$

again with a difference clearly insignificant.

Hence, it may be generally concluded that, except at very low temperatures or on a planet or star with a considerably higher gravitational constant, gravity cannot produce any appreciable variation with depth in the composition of a fluid mixture. It is possible, however, that in a centrifuge *effective* gravity constants may be obtained such as to make the effect observable.*

Finally, we shall outline the method of treating binary mixtures of compressible fluids. We note that equation (13′) implicitly gives the distribution function, in the general case, except for the constants c_i. For the binary case, these constants may be determined as follows:

We know that at $z=0$, $p=Mg+p_0$ where M is the total mass of the liquid in the column of height, h, and unit cross section; also, at $z=h$, $p=p_0$. We therefore have

* This possibility was kindly suggested to us by Dr. A. G. Loomis of this laboratory.

$$\left.\begin{aligned} \tilde{n}_1(0) &= c_1 e^{-k/g b_1(Mg+p_0)}; & \tilde{n}_2(0) &= c_2 e^{-k/g b_2(Mg+p_0)} \\ \tilde{n}_1(h) &= c_1 e^{-k[b_1(p_0)/g+w_1 h]}; & \tilde{n}_2(h) &= c_2 e^{-k[b_2(p_0)/g+w_2 h]}. \end{aligned}\right\} \tag{39}$$

As $\tilde{n}_1(0) + \tilde{n}_2(0) = 1$ and $\tilde{n}_1(h) + \tilde{n}_2(h) = 1$, c_1 and c_2 can be expressed directly in terms of the known constants of the mixture, if we put into the above expressions the proper forms of the functions $b_1(p)$ and $b_2(p)$.

We next determine the pressure, p, by the relation;

$$c_1 e^{-w_1 z + b_1(p)} + c_2 e^{-w_2 z + b_2(p)} = 1. \tag{40}$$

When it is difficult to obtain an algebraic solution of this equation, for $p = p(z)$, a graphical solution will always be possible. When $p(z)$ is known, it may be put back into (13′), and we shall then have the desired solution to the problem, namely, the mol-fractions $\tilde{n}_i$ as a function of z. The individual molar concentrations, n_i, are then given by the general relation, already used in Eq. (20):

$$n_i = \frac{\tilde{n}_i}{\sum_j \tilde{n}_j v_j}. \tag{41}$$

With the aid of these formulae, $\tilde{n}_i(z)$ and $n_i(z)$ may be determined for any particular case of a binary mixture of compressible fluids. Of course, the mixture of incompressible fluids is a special case of these, but the previous development has been given as it illustrates more clearly the general problem of the incompressible fluids.

The writer is indebted to Dr. P. D. Foote and Mr. W. O. Smith for suggesting this problem and to Drs. A. E. Ruark and L. Shereshefskey for the opportunity of discussing the problem with them.

THE RECOMBINATION OF IONS IN AIR AND OXYGEN IN RELATION TO THE NATURE OF GASEOUS IONS

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Abstract

Coefficient of recombination of ions produced by x-rays as a function of the age and initial concentration of the ions. Measurement of the coefficient of recombination of ions in air and oxygen has been continued, with an improved form of the apparatus previously described by L. C. Marshall. Marshall's results in air have been checked, showing a sharp initial drop in the coefficient α for short time intervals ascribed to initial non-random distribution of the ions. Further measurements at longer time intervals have been made, using a new system of calculation whereby α is found as a function of τ, the age of the ions, rather than t, the total time of recombination. In this case α does not drop to a constant value of about 0.8 to 0.9×10^{-6} as indicated by Marshall's results, but continues to drop off to values of 0.5 to 0.6×10^{-6} after the ions have aged for one second, and 0.3 to 0.4×10^{-6} after two seconds. This is for a high initial concentration of ions of about 3.5×10^{6} ions per cm^3. With an initial concentration of 1.55×10^{6} ions per cm^3, α drops only to 1.15×10^{-6} after a time of one second. In pure oxygen the values of α are in general higher than the corresponding ones for air, although they become equal at low inital concentrations.

Interpretation of results and the absolute value of the coefficient in air. The results may be explained by assuming that heavy slow-moving ions are formed in increasing amounts as time goes on by reaction with impurities present. The faster ions are constantly being removed at a high rate by recombination, leaving the slow ions behind with a resulting increasingly low coefficient of recombination. It is possible that the ionizing agent produces nitric oxides, O_3 or H_2O_2, which load up the ions. It is impossible to set accurately an absolute value of α in air, due to two disturbing factors: initial non-random distribution producing abnormally high values of α at short time intervals, and the loading up of the ions with impurities producing abnormally low values of α at long time intervals. At a time where these two factors have a minimum effect α has the value $1.4\pm0.1\times10^{-6}$, which is set as the closest approximation to an absolute value.

Introduction

RECENTLY in this laboratory L. C. Marshall[1] measured the coefficient of recombination of ions in air and argon using a new direct method with x-rays as a source of ionization. His results showed that the coefficient α given by the equation $dn/dt=-\alpha n^2$ is not a constant as has generally been supposed with a value about 1.6×10^{-6} for air but is a function of three factors: (1) the time of x-ray exposure t'; (2) the initial ion concentration n_0; (3) the time of recombination t. He found that α dropped from a value of 4.0×10^{-6} at short times of recombination to an apparent nearly constant value of about 0.8 or 0.9×10^{-6} at time intervals of about one second. Also, the value of α was in general higher for short times of x-ray exposure and small

[1] L. C. Marshall, Phys. Rev. **34**, 618 (1929).

initial concentrations of ions. The high values at short time intervals were shown by experiment and also by the theory of Loeb and Marshall[2,3] to be due to the initial non-random distribution of the ions which results from their formation in pairs along a β-ray track. The theory indicates that after a time interval of about 2.25×10^{-3} seconds, the value of α should become constant since by that time the ions would attain random distribution due to their heat motions.

The work has been continued by the writer in air and oxygen with essentially the same apparatus as that used by Marshall, although with important improvements in some details and particularly using a new method of measurement and calculation. These results show that the value of α does not become constant after a short time as indicated by Marshall's results but continues to fall off quite rapidly as the ions become older. This leads to important conclusions concerning the nature of gaseous ions.

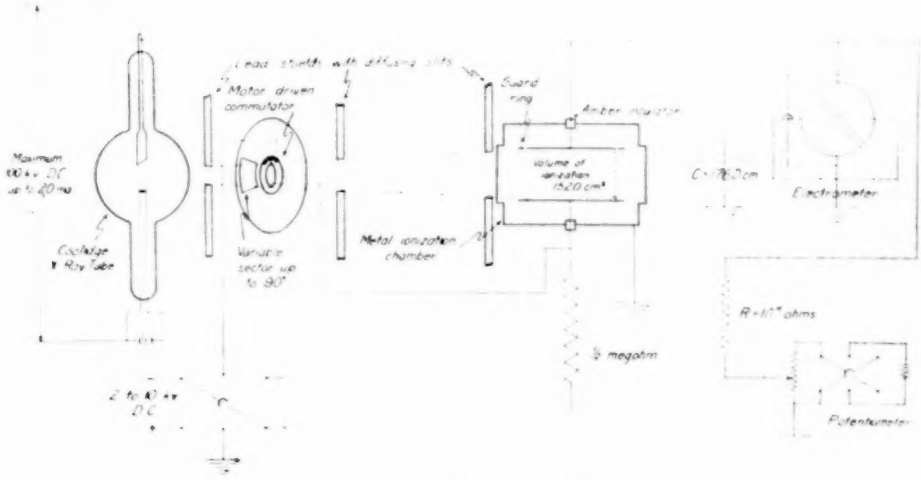

Fig. 1. Diagram of apparatus.

Method of Measurement

The apparatus and system of measurement has previously been described by Marshall.[1] The essential features are shown in Fig. 1. D.C. potential is applied to the Coolidge x-ray tube by means of a transformer, kenotrons and filter system not shown in the diagram. The x-rays pass through a solid brass rotating disk which has a variable sector from 0° to 90° cut in it, thus producing a flash in the metal ionization chamber. The beam of x-rays is defined by three lead slits and passes through almost two meters of air and an aluminum window before reaching the chamber. The beam is thus sharply defined and nearly homogeneous. The shaft carrying the sector also carries an adjustable commutator by which potentials of 1000 to 10,000 volts may

[2] L. B. Loeb and L. C. Marshall, Jour. Franklin Inst. **207,** 371 (1929).
[3] L. B. Loeb, Trans. Am. Electrochem Soc. **LV,** 131 (1929).

be applied to the lower plate of the chamber. The high field almost instantly sweeps all the ions of one sign to the upper plate at any desired time after the x-ray beam has been cut off by the brass disk. The lower plate is also connected to ground through a one-half megohm resistance so that its potential becomes zero immediately after the brush breaks contact with the commutator segment.

Since the upper plate must also be kept at zero potential during the flash time and time of recombination, a neutralizing mechanism is used to prevent a charge from building up on the plate and electrometer system as a result of the repeated flashes of x-rays. For this the alternate system described by Marshall is used. A current of opposite sign to that collected on the upper plate of the chamber is forced through the high resistance leak R by means of a voltage applied from a potentiometer. Thus, when the electrometer deflection is zero, the two currents are neutralizing each other and the voltage

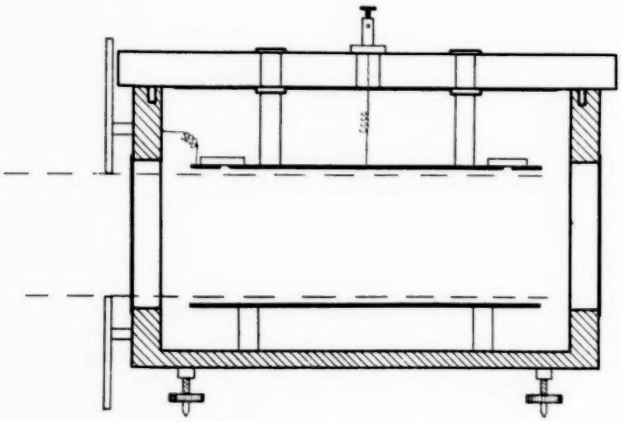

Fig. 2. Ionization chamber.

read directly from the potentiometer will be proportional to the ionic current.

It may be noted that difficulty was encountered in constructing a high resistance leak of the order of 10^{10} ohms which would remain constant over a period of several hours. Experiment showed that an India ink line drawn on typing paper and enclosed in an airtight vessel containing a small amount of P_2O_5 to remove the moisture, was satisfactory. Such a leak exhibits no polarization and stays constant well within 0.5 percent.

The only major change made in the apparatus used by Marshall was the substitution of a new ionization chamber allowing much greater volume of ionization (See Fig. 2). It consists of rectangular brass plates in a heavy brass box fitted with aluminum windows through which the x-ray beam passes. An important feature of the chamber is the plate glass cover to which the upper plate and guard ring are attached by means of amber insulators. The cover is sealed on by means of stopcock grease, a double seal with a groove between being employed to prevent the diffusion of stopcock grease vapor

into the chamber. The stopcock grease is employed only in the outer seal, all excess grease being forced either outside or into the groove. The total volume of ionization is 1520 cm³ compared to 63 cm³ in Marshall's apparatus. The advantages of this large volume are: (1) the ionic currents are much larger and can be measured more accurately; (2) the volume can be determined more accurately and diffusion plays a smaller though still appreciable role. In this connection it may be noted that the x-ray beam extends well beyond the sides of the plates; so that only diffusion toward the plates must be considered; not that toward the sides or ends.

The air and oxygen used in the ionization chamber were purified according to standard technique, all dust, moisture, CO_2 and organic vapors being removed by passage through glass wool, $CaCl_2$, sodium calcium hydrate, P_2O_5, and two liquid air traps. Special care was taken to remove organic substances by cleaning the metal chamber thoroughly with cleaning solution.

In calculating α the integrated form of the well-known equation,

$$\frac{dn}{dt} = -\alpha n^2 \tag{1}$$

is used, where n is the number of ions of either sign per cm³. Integration gives:

$$\alpha = \frac{1}{t}\left(\frac{1}{n} - \frac{1}{n_0}\right) \tag{2}$$

where t is the time of recombination, n_0 is the number of ions per cm³ at $t=0$ and n is the number of ions left after time t. Inserting the experimental constants Eq. (2) becomes:

$$\alpha = \frac{1.59 \times 10^{-19} RNV}{\epsilon} \frac{1}{t}\left(\frac{1}{r} - \frac{1}{r_0}\right) \tag{3}$$

where R is the value of the high resistance leak in ohms, N is the number of revolutions per second of the commutator, V is the volume of ionization, ϵ is the e.m.f. of the neutralizing potentiometer battery in volts, and r and r_0 are the direct potentiometer readings at the time $t=t$ and $t=0$ respectively.

In the method of calculation one important change is made from that used by Marshall who measured n_0 the number of ions at the instant the x-ray flash was cut off, then n the number left after varying time intervals t. α was calculated between these two limits thus giving an average value over the whole time of recombination. In the present work values of n_0, n_1, n_2, $\cdots$ are measured at short intervals of time 0, t_1, t_2, $\cdots$. Then α may be calculated between any two of these intervals. That is, Eq. (2) becomes of the form:

$$\alpha = \frac{1}{t_p - t_q}\left(\frac{1}{n_p} - \frac{1}{n_q}\right). \tag{4}$$

This allows α to be studied as a function of the age of the ions rather than as a function of the time of recombination after the x-rays are cut off. Setting τ as the average age of the ions over any period of recombination $t_p - t_q$ and assuming $\tau = 0$ at $t = 0$ we have:

$$\tau = t_q + \frac{t_p - t_q}{2}. \tag{5}$$

If $t_p - t_q$ is a short time interval compared to the maximum time allowable at any particular commutator speed, τ is a fairly accurate measure of the age of the ions and the variation of α with τ can be studied.

Results

The first series of runs were taken as a check on Marshall's work and show results similar to his, α being plotted as a function of t the time of recombination (see Fig. 3). Each succeeding run was taken with the commutator speed one-half that of the previous run. These show the sharp initial drop due to the non random distribution of the ions with the apparent flattening out of

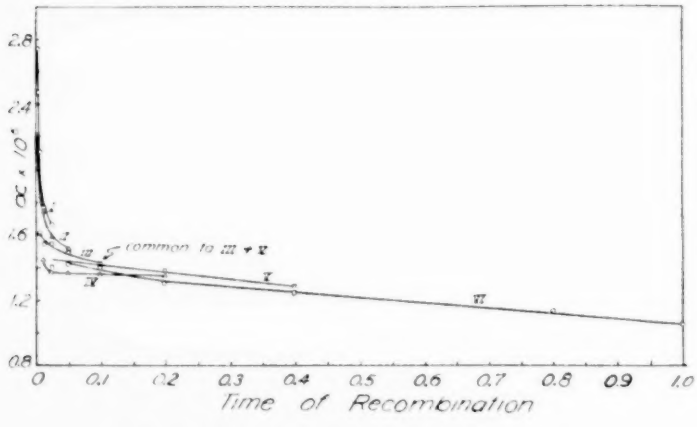

Fig. 3. First six runs corrected for diffusion.

the curves at longer time intervals. The final value at one second is about 1.03×10^{-6} compared to Marshall's value of 0.9×10^{-6}. This is due to a very short time of exposure (0.01562 seconds which was kept constant throughout the series of runs by narrowing the sector) and a resulting low initial concentration of the ions. The matter of initial concentration is important even at long time intervals as will be seen later.

All later runs were taken by measuring n at short intervals of time thus making it possible to calculate α as a function of τ the age of the ions, as well as a function of t the time of recombination. All the curves (Fig. 5) show without exception a continued drop in α up to a time of two seconds, the maximum time which could be studied. At the end of these long time intervals α still shows no indication of becoming constant although the slope of the curves gradually decreases.

Fig. 4 shows a comparison for one particular run of the two methods of calculating α. In the upper curve, α is plotted as a function of the time of recombination, in the lower curve as a function of τ the age of the ions. In the lower curve α drops more sharply than in the upper. In other words, Marshall's results gave an average high value of α rather than the true value at any particular time. However, on the magnified scale of Fig. 4, α still drops quite sharply even with Marshall's method of calculating, while it appeared to be nearly constant on the scale used in Fig. 3.

Values of α calculated as a function of τ do not lie as close to a smooth curve as those calculated as a function of t. (See Fig. 4). This is because α is obtained for comparatively small differences in the potentiometer readings, especially at the later time intervals when the concentration of ions

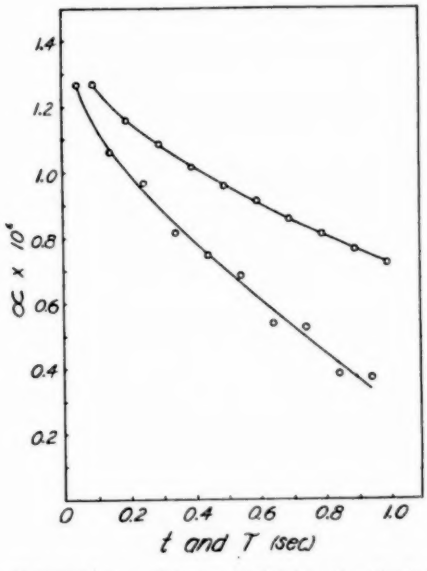

Fig. 4. Comparison of two methods of calculating α.

has become small and very little recombination takes place. Thus small errors in the potentiometer readings may result in large errors in the calculated values of α. However, the points show a definite trend in every case. This is more important than the absolute values since a final definite value of α does not seem to exist.

Fig. 5 shows the complete results for all the runs taken over the longer time intervals in air and oxygen. α is plotted against τ, the age of the ions, and the curves are all averages of values taken from two or more runs which may vary by considerable amounts due to an overcorrection for diffusion at the longer time intervals which will be discussed later. The dotted lines show the results in oxygen and the full lines those for air.

Curve I is a run taken with the commutator revolving at the rate of two revolutions per second; curve II, one revolution per second; curve III 0.5 revolutions per second; curve IV 0.25 revolutions per second; all at rather

high intial ion concentrations varying from 2.5 to 3.5×10^6 ions per cm^3. Curve V is taken in air at 0.5 revolutions per second corresponding to curve III, only in this case the initial concentration was reduced to 1.55×10^6 ions per cm^3 compared to 3.5×10^6 for curve III. As can be seen, the values of α for the low concentration are much higher than those for high concentration although the slope of the curve is approximately the same in each case.

Curves VI, VII and VIII are those for pure oxygen; VI corresponding to III for air, VII corresponding to V and VIII corresponding to IV. Curve VI is much higher than the corresponding curve III for air at the same initial concentration. For low concentrations the oxygen and air curves (V and VII) are approximately the same although the points do not fall on a smooth curve due to the extreme difficulty of measuring the coefficient accurately at these low concentrations. The trend is very definite however,

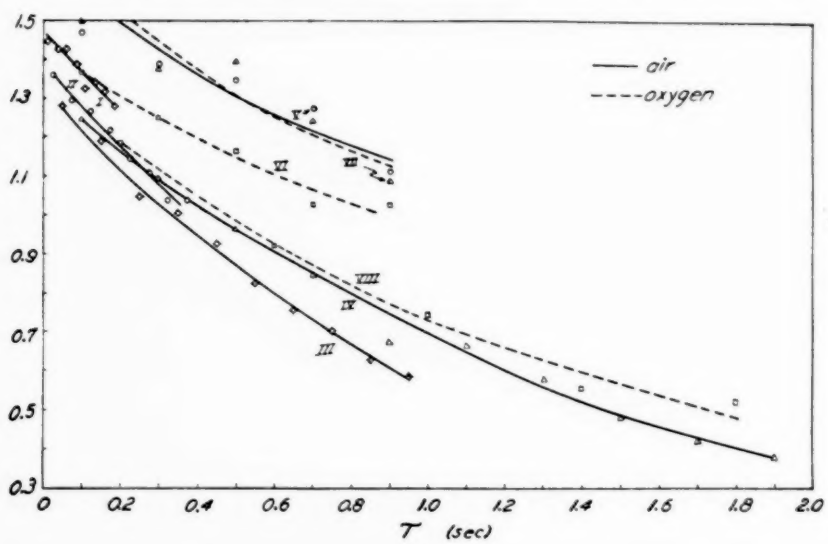

Fig. 5. Complete results for all runs taken over the longer time interval in air and oxygen.

and shows the slope to be about the same as for the curves taken at higher concentrations. Curve VIII for the longest time intervals in oxygen is only slightly higher than the corresponding curve IV for air although there is a distinct difference.

One question which must be considered in connection with these results is the correction for diffusion. Two types of runs were made: one with the beam of x-rays grazing though not touching the plates; so that the whole volume between the plates was ionized; and another with the beam about one centimeter from the plates. In general if no diffusion correction is made, the values of α obtained in each case are nearly the same. If, however, correction is made for diffusion, the values are higher when the beam is one centimeter from the plates, especially at the longer time intervals. This results from the fact that the correction is in the opposite direction in the two cases.

For the case when the beam grazes the plates, a certain number of ions diffuse to the plates during the time of recombination and are thereby lost. This loss is in addition to the loss due to recombination. The number lost by diffusion may be calculated, and this number then added to the measured value n_p at the time t_p to give the true value due to recombination alone. The number diffusing to the plates in time $t_p - t_q$ is given by

$$2n_pA[(\overline{\Delta x})_p - (\overline{\Delta x})_q] \text{ where } (\overline{\Delta x})_p = \left(\frac{4Dt_p}{\pi}\right)^{1/2} \text{ and } (\overline{\Delta x})_q = \left(\frac{4Dt_q}{\pi}\right)^{1/2}$$

n is the number of ions per cm^3 of either sign, A is the area of each plate, $\overline{\Delta x}$ is the average distance an ion diffuses in the time t derived from the Brownian movement equation,[2] and D is the coefficient of diffusion having a value about 0.047. The number

$$2n_pA\left[\left(\frac{4Dt_p}{\pi}\right)^{1/2} - \left(\frac{4Dt_q}{\pi}\right)^{1/2}\right]$$

being added to the measured value of n_p serves to reduce the uncorrected value of α by as much as ten percent.

Marshall has derived a rather complicated equation for the case when the beam is some distance from the plates but this is not readily applicable when α is calculated as a function of τ rather than t. In this paper therefore, a correction is made assuming a swelling of the volume of ionization due to diffusion which gives approximately the same results as Marshall's equation. In calculating α at any time τ the volume is assumed to be:

$$V = V_0 + 2A(\overline{\Delta x})_\tau = V_0 + 4A\left(\frac{D\tau}{\pi}\right)^{1/2}.$$

Since V occurs in the numerator of Eq. (3) this increases the value of α over that calculated without the diffusion correction.

From the fact that the diffusion correction throws the values of α as much as twenty percent apart at the longest time intervals there is apparently an overcorrection for this effect in the equations and values used. This would follow if the coefficient of diffusion becomes less for the ions remaining after long time intervals. Other factors may further reduce the actual rate of diffusion, but from a kinetic theory standpoint a correction like that indicated is necessary. As it does not seem justifiable to omit the correction, all the results are calculated in this manner and the average of the two types of runs is taken in plotting the curves in Fig. 5. The absolute value of α in the curves may be too high or too low by several percent especially for large values of τ since the correction for the case when the beam is one centimeter from the plates is greater than for the case when the beam is grazing the plates. However, the important fact remains that in every case, no matter whether a diffusion correction is made or not, the value of α still drops off continuously with the aging of the ions.

Summary of Results and Conclusions

From the curves in Fig. 5 the behavior of α may be summed up as follows:

(1) α is not a constant as has always been supposed, but beyond the sharp initial drop due to the non-random distribution of the ions, the curves continue to drop indefinitely as the ions age. At the end of one second the value of α is 0.5 to 0.6×10^{-6}; at the end of two seconds, 0.3 to 0.4×10^{-6}.

(2) The lower the initial concentration of ions, the higher the value of α after random distribution has been attained. The value for an initial concentration of 1.55×10^{6} ions per cm^3 drops to about 1.15×10^{-6} at the end of a second compared to about 0.6×10^{-6} when the initial concentration is 3.5×10^{6} ions per cm^3. However, the slope of the curves is about the same in each case.

(3) The values of α in pure oxygen are in general higher than the corresponding ones in air although they become equal when the initial concentration of the ions is small. The slope of the curves is still the same indicating that the same type of aging effect is taking place.

At first glance it would seem impossible to explain these results by any reasonable assumption. *However, the whole situation becomes clear at once if it is supposed that as time goes on some of the ions form clusters with the impurities present.*

Although special care was taken to remove organic vapors such as ether, alcohol, stopcock grease, etc., which are known to affect the nature of the ion, the number of these heavy molecules present was probably comparable to the number of ions. In addition, water vapor may be present coming from the walls of the metal chamber and there is the possibility that the intense hard x-rays form small quantities of nitric oxides, O_3 or H_2O_2. Any of these impurities might form large ion clusters in increasing quantity during the time of measurement. The method is particularly sensitive to impurities as the small, fast moving ions are removed first by recombination leaving the heavier ions as time goes on. Hence α drops continuously.

The supposition that impurities formed by the x-rays form clusters is in agreement with the work of Tyndall, Grindley and Sheppard,[4] also that of Erikson.[5] Erikson showed definitely that the presence of β-rays from radium emanation tubes formed impurities which hastened the aging of the ions so that clusters formed in about 0.001 second. Passage of the gas through a metal ionization chamber which had not been thoroughly cleaned also hastened the aging although to a lesser degree. If neither the β-rays or metal ionization chamber were present there was no appreciable aging effect up to 0.1 second.

Since measurements of the coefficient of recombination in pure oxygen give in general higher values than in air, it would seem that the extremely low values in air are due in part to nitric oxides. The fact that low initial ion concentrations give higher values of α than high initial concentrations is

[4] Tyndall, Grindley and Sheppard, Proc. Roy. Soc. **A121,** 125 (1928).

[5] H. A. Erikson, Phys. Rev. **34,** 635 (1929).

further evidence that clusters of some sort are forming and that the more intense the ionizing agent the more impurities there are present to retard recombination.

It has always been a moot question as to the true nature of ions in gases of normal purity such as are used in this experiment. Practically the only evidence on this subject is from mobility measurements. Erikson's well-known aging of the positive ions gives an indication of clustering and Loeb's measurements in mixtures show definitely that clustering occurs in some gases. Apparently in other gases the ions may consist of single molecules or at any rate small aggregates. However, the evidence from mobility measurements is incomplete in two respects: first because the measurements are generally made within a time interval of less than one tenth of a second after the ions are formed, and second because the mass factor is an unimportant one in mobility; i.e., the mobility is decreased very little by a considerable increase of mass.

The coefficient of recombination measurements are more reliable since in this case the ions can be studied up to time intervals of two seconds after they have had a chance to collide with all kinds of impurities and the faster ions have been weeded out by recombination. In addition, the mass factor is much more important than in mobility or diffusion. On J. J. Thomson's[6] theory of recombination which Loeb and Marshall[2] have shown to be a correct approach to the problem, α is proportional to the velocity of thermal agitation of the ions. The velocity of thermal agitation is in turn inversely proportional to the square root of the mass. The better of two equations as given by Loeb and Marshall after inserting the various constants turns out to be:

$$\alpha = 1.9 \times 10^{-5}\left(\frac{273}{T}\right)^{3/2}\left(\frac{1}{M}\right)^{1/2}\epsilon$$

where T is the absolute temperature, M is the molecular weight of the ions, and ϵ is the probability that recombination will occur if the ions approach each other within a defined distance d. For the case of air or oxygen at room temperature and 760 mm pressure the theory gives ϵ a value of about 0.9 which, however, may be too high. T is about 295° so that the equation reduces to:

$$\alpha = 1.51 \times 10^{-5}\left(\frac{1}{M}\right)^{1/2}.$$

If α has a value of 0.4×10^{-6} which is the lowest observed in this work, it turns out that M the molecular weight of the ions is about 1400. This seems unreasonably high but is not inconceivable if there were a large cluster of heavy molecules. The equation, however, is correct only to the roughest approximation and probably gives high values of α. As a result, the mass, which varies inversely as the square of α may be much less than 1400.

[6] J. J. Thomson, Conduction of Electricity through Gases, III Edition, Cambridge 1928.

The only conclusion which can safely be drawn is that little is actually known concerning the nature of gaseous ions, but that in gases of normal purity that are ordinarily used in gas ion work, clusters of large mass are formed, due probably to the effect of the ionizing agent. The process of cluster formation and weeding out of the faster ions by recombination continues for at least two seconds after the ions are formed. The exact nature and true mass of these clusters cannot be accurately determined owing to the lack of a completely satisfactory theory.

The absolute value of α in air. It appears to be of considerable interest to know the absolute value of α in air for use in numerous calculations. It is evident from the results in this paper that there are two factors which make it impossible to set an accurate absolute value. The first factor is the initial non-random distribution of the ions which produces very high apparent values of α at short time intervals and the second is the loading up of the ions with impurities and selective recombination which produces abnormally low values of α at long time intervals. Probably the closest approach to an absolute value is at a time when the ions have nearly attained random distribution but clustering and elimination of the faster ions has not yet played a major role. In other words, a point must be chosen on the curves in Fig. 3 where the sharp drop in α ends and the more gradual steady drop due to clustering begins. Such a point appears to lie between 0.05 and 0.1 seconds where the value of α is $1.4 \pm 0.1 \times 10^{-6}$. This is not much different from the commonly accepted value of 1.5 or 1.6×10^{-6} which has been determined by earlier investigators under conditions where, in general, these important disturbing factors have not been detected, or at any rate not clearly differentiated. The value of 1.4×10^{-6} for air may then be used with some degree of confidence under conditions where the ions have attained random distribution but have not aged more than one-tenth of a second.

In conclusion, the writer wishes to express his appreciation to Dr. Marshall who designed and constructed the fundamental parts of the apparatus; to Mr. G. P. Kraus of the shop who accomplished a difficult piece of work in building the ionization chamber; and to Mr. N. E. Bradbury who assisted in taking some of the later readings. Particularly, the writer wishes to thank Professor Loeb for his unfailing interest in the work and for his suggested explanation of the experimental results.

At present, the measurements are being continued in other gases, particularly argon and hydrogen.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Reflection of Positive Ions by Crystals

Further experiments on the reflection of hydrogen positive rays from crystals similar to those described in The Physical Review for December 1, 1929 have shown that the phenomenon is more complex than might have been expected. More than a hundred photographs showing reflected rays have been obtained under various conditions, and show several features of interest. Great differences have been found in the reflecting powers of different samples of calcite. Two were found that gave strong reflected rays when the glancing angle was less than two degrees. The images obtained on Schumann plates placed at right angles to the beam may be properly termed reflection patterns, as they show considerable complexity, vary in a regular manner with the angle of incidence, and can be reproduced at will with the same setting of the crystal and speed of the rays. Six other calcite crystals gave reflection patterns containing fewer lines or lines on a fogged background. Reflected rays were also observed with a diamond which was kindly loaned by Dr. D. Cooksey. A natural cleavage face of this diamond had been used in experiments on the reflection of gamma-rays. A highly polished face gave indistinct patterns on a fogged background. Clear lines were obtained from two other faces, one of which was the natural cleavage face, and the other a face that had been cut and appeared rough due to the saw marks. No reflected rays were found in a few trials with rock-salt galena and magnetite.

The strongest parts of the patterns are produced by rays that have energies corresponding to more than six thousand volts Slower rays may be present in the original bundle, as shown by a positive ray analysis, but they are not reflected as strongly as the faster rays. With a low potential on the discharge tube, the reflection pattern lacks certain of the parts that appear with high potentials. A positive-ray analysis of the ions reflected from one of the calcite crystals showed that in addition to the hydrogen atoms previously reported, all the positive ions in the original bundle are present in the reflection patterns, viz.: hydrogen molecules, triatomic hydrogen molecules and heavier ions that are probably oxygen atoms. With the present resolution the various ions are superimposed in the streaks or lines formed by the reflected rays of various velocities.

The dependence of the angle of deviation by the crystal on the energy of an ion rules out the possibility of ascribing the reflection to the deviation of particles by electrostatic forces which would require the reflected rays of various velocities to lie in a plane and to have angles of deviation inversely proportional to the energies of the particles. In most cases the reflected rays of different velocities do not lie in planes as they give curved images on the plate and in the cases where a straight line is formed the deviation is not inversely proportional to the energy but is a linear function of the reciprocal of the velocity. Charges would not be expected to accumulate on the crystal because of the secondary electrons liberated by the bombardment of metal parts near it and its uncharged condition is shown by the fact that those rays which just pass over the crystal without hitting it are undeflected. The small penetration of ions into matter as compared with electrons of the same equivalent wave-length suggests that energy changes at the surface or inside the crystal will have to be taken into account in a complete theory. The important factor in determining the angles may be a quantity

analogous to a refractive index which would depend on the energy of the ion and its alterations.

Small changes in the angle at which the incident rays hit the crystal produce a regular series of changes in the directions of the deflected rays. At nearly grazing incidence on one of the calcite crystals with the rays parallel to an edge of the cleavage rhomb there was a fan-shaped arrangement of the reflected rays in eight or more radial lines of different intensities. As the angle was made steeper the lines formed by the reflected rays of various velocities shifted towards the normal to the crystal surface and became curved the intensities altered and new curved lines appeared at the sides making the patterns more complex and more symmetrical. This change was produced by an increase of only one degree. With a second calcite crystal which was turned so that at grazing incidence the rays made an angle of about fifteen degrees with an edge of the cleavage rhomb clear patterns were obtained which had an unsymmetrical character. These patterns as well as those from the diamond also changed in a regular manner with small increases in the angle of incidence. The dependence of the angles of reflection on the angle of incidence and on the velocity of the rays suggests very strongly that a theory of the phenomenon will have to contain other elements besides particles and the forces exerted on them by electric and magnetic fields.

A. J. DEMPSTER

University of Chicago
April, 1930.

High-Voltage Tubes

We have found that the internal shattering and puncturing of Pyrex high voltage tubes of the cascade type described in the Physical Review of January 1 is entirely eliminated if the glass is "heat-worked" throughout. Since last autumn we have been using tubes made by blowing a series of "bubbles" which comprise the cascade sections at proper intervals along a piece of Pyrex tubing using a glass lathe for holding the work. In other respects the tube construction and shielding have been similar to that previously described except that tungsten instead of wax seals were used and the electrodes were shorter. Shattering and puncture finally occurred with most of our tubes in the necks between bulbs ("bubbles") although such tubes were operated to over 1600 kilovolts by careful "seasoning" and by short-circuiting sections which shattered before these had progressed to actual puncture. It was then found that if the glass tubing was first worked at all points (by heating and alternately blowing and contracting as in working a glass seal or joint) and then formed into bubbles and necks and the electrodes assembled no shattering took place when the tube was used. In two months of very severe tests on a series of such "heat-worked" tubes we have not been able to produce any shattering or puncturing with our Tesla coil voltages. One such tube of 14 sections, 135 cm overall, was operated up to 1950 kolovolts (at about one spark per second) where gassing set in due to slightly contaminated electrodes. This type of limitation by gas is the only one we experience with these tubes and our vacuum technique can be improved considerably when higher voltages are desired. An ionization-gauge near the pumps usually reads about 10^{-5} mm Hg equivalent air-pressure. We find that every tube which is assembled using reasonable precautions against contamination expecially by water-vapor, can be relied on to go to voltages of 1,000 to 2,000 kilovolts, depending on the number of sections, the ground-point, and the success in avoiding contamination, which usually shows up as a discoloration of the out-gassed electrodes.

These tubes have been operated as high as 1500 kilovolts without a potentiometer, that is, with all except the end-electrodes electrically floating. We made the accidental discovery on several occasions that some of our potentiometer units had been broken while we were running a tube, without our knowing of their failure until afterwards, no trouble having been noted with the tube. When all of the potentiometer units were removed, the tube still operated without severe flashing, although the voltage-distribution was obviously very non-uniform. Brasch and Lange (Naturwiss. January 3, 1930) have already reported the successful operation of a somewhat similar "floating-electrode" tube. Whether or not a filament is used in a tube makes no detectable difference in its behavior or flashing, at least up to 1500 kilovolts at one spark per second, nor has any effect of the filament

been noted with 120 sparks per second up to 800 kilovolts, which voltage has happened to be the maximum available with 60-cycle excitation of the condenser at the time of these tests, due to temporary power-limitations.

We are now using tubes of 12 sections placed inside of a Tesla coil 6 inches in diameter and 38 inches long, each electrode being connected to a tap on the winding of the coil. The coil itself shields the tube from ground, and distributes the voltage. A tube of this type, *with one end grounded*, has been operated to 1900 kilovolts at one spark per second, and to 1600 kilovolts at 120 sparks per second, at which voltage the tube operated perfectly; primary power was again the limitation. Insulation difficulties are also serious at these voltages above ground. Experiments are in progress on direct measurements of the output from these tubes of the expected radiations and "rays" of radioactive energy-equivalents, the results of which we hope to report shortly.

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L. R. HAFSTAD
O. DAHL

Department of Terrestrial Magnetism,
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May 6, 1930.

Photoelectric Effect and the *J* Phenomenon

In the issue of the Physical Review for May 1, 1930, appears a paper by E. Marx describing "A new photoelectric effect in alkali cells" wherein that author investigates changes produced in the limiting potential acquired by an insulated alkali electrode, by varying the composition of the incident radiation. Although these experiments constitute the first systematic study of the phenomenon in the optical region, an analogous investigation was carried out with x-rays some years ago by C. G. Barkla. I quote from one of the latter's notices (Nature, March 27, 1926, p. 448)—"The ionization produced by a heterogeneous beam of x-rays in a gas, or the electronic emission from a metal plate, (measured by ionization outside the plate) may be abruptly and enormously increased either by (*a*) superposing on that beam a very feeble radiation of slightly shorter wave-lengths, or (*b*) by taking away from the complex radiation a very small amount of the radiation of longer wave-lengths, as by filtering; that is, either by adding higher frequency radiations to or eliminating lower frequency radiations from the beam, the same effect is produced; namely, a sudden large increase in the ionization. The magnitude of a sudden increase may be from 100 to 150 percent of the original magnitude. This is the *J* ionization produced by the *J* photoelectric emission accompanying the *J* absorption."

Since the independent variable (composition of the incident radiation) is the same for both cases, they deal presumably with the same effect, and it should be legitimate to compare the results, although an extrapolation from the optical to the x-ray region must be made with caution. This comparison is difficult, since it is unlikely that the experimental arrangements were the same for both. In Marx's work, the alkali electrode was insulated, and the removal of some of the red from an incident beam of white light caused an increase in the limiting potential acquired. On the other hand, in Barkla's experiment, the photoelectric plate was probably kept at a constant potential, and he observed that the removal of some of the long wave-length radiations from the beam of x-rays caused an increase in the ionization due to photoelectrons. Barkla interprets his result as a manifestation of some unexplained interaction between the component radiations in the incident beam, which causes a fundamental change in the amount or in the nature of the photoelectric emission. This is not necessarily inconsistent with the experiments of Marx, but it is not one of the assumptions of the tentative theory which he offers. Other possible suppositions as to Barkla's experimental arrangement lead also to conclusions which are at variance with the theory of Marx. At present all that can be deduced is that the four items (*a*) the experiments, (*b*) the theory of Marx, (*c*) the experiments, (*d*) the theory of Barkla, are not consistent.

I am not aware that Barkla's observation has ever been verified. It is possible that a series of varied experiments of this nature might throw some light on the elusive *J* phenomenon.

THOMAS H. OSGOOD

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Pittsburgh, Pennsylvania,
May 15, 1930.

The Origin of O^{17}

In the Physical Review of April 1 Harkins and Schuh have considered the possibility of all the o^{17} atoms in the earth's crust and atmosphere having been formed by close collisions of alpha-particles with the nuclei of nitrogen atoms as revealed by the cloud tracks. Assuming that the ratio $O^{17}:O^{16}$ atoms is the same in the crust as in the atmosphere and that the known nitrogen and radium contents are uniformly distributed in the crust they estimate that the necessary lapse of time would have been about 10^{18} years which is an impossibly great age for the earth.

At about the same time the writer made (Minnesota Technolog **10,** 240 (1930)) a similar calculation for the atmosphere alone by using its known radon content of 10^{-10} curie per cubic meter. The result is about 10^{14} years required. Since this also represents an apparently excessive age one is inclined to seek auxiliary means of production. A former content of U-Ra-Rn higher than at present suggests itself but seems improbable as one would then expect to find higher Pb:U ratios than those actually found in nature.

From Harkins and Schuh's calculation it is evident that oxygen liberated from the crust would diminish the relative content of O^{17} in the atmosphere. However if instead of a uniform distribution of uranium and nitrogen in the crust we consider concentration in the form of high grade uranium ore and an enhanced concentration of nitrogen in the ore the rate of O^{17} production would be increased. Hillebrand ((W. F. Hillebrand U. S. Geol. Survey Bull. **78,** 43 (1891); Am. J. Sci. **40,** 384 (1890)) did find a striking association of nitrogen and uranium. Whether this could be a large source of O^{17} would of course depend on the size of such deposits. This would be difficult to estimate and it appears unnecessary to consider it further in this connection since the following simple considerations show it to be highly improbable that any important fraction of o^{17} in the atmosphere can have been generated on the earth either in the crust or in the atmosphere itself by alpha-ray bombardment.

About 100,000 alpha-particles are required for each nuclear encounter with nitrogen. Therefore the ratio of He to O^{17} generated would be 100,000 He:1 O^{17}. In the atmosphere the actual ratio is about 1 He:5 O^{17}. We can hardly conceive any natural process that would have achieved a change of 500,000 fold in the ratio of the two gases.

If we reverse the calculation and assume with Jeans (Jeans' Dynamic Theory of Gases, 1921, p. 345-6) no diffusion of helium away from the upper atmosphere then for 100,000 He atoms there would be only one O^{17} atoms of the assumed origin, or only about two millionths of the O^{17} atoms actually found by the band spectrum method.

As a matter of fact there are good reasons for believing that at least several fold as much helium *has* diffused "out at the top" as now remains, since that many fold have been liberated into the atmosphere by erosion, etc. The writer would point out that Jeans' denial of loss by diffusion is based wholly on thermal diffusion; whereas light gases like hydrogen and helium in the upper atmosphere can absorb radiation which upon conversion into translational energy would give them a velocity quite beyond that corresponding to thermal equilibrium with the surroundings and thus allow their escape. This process would therefore raise the O^{17} ratio by lowering the helium. While it may have taken place to an extent several times the present helium content of the atmosphere, it would be difficult to believe that it might have occurred to an extent of 500,000 fold, which would be necessary to have established the present He:O^{17} ratio.

S. C. Lind

School of Chemistry,
University of Minnesota,
May 9, 1930.

Paschen-Back Effect on the Line Spectra of Solids

In a work which we shall publish soon,[1] we have been able to assign a number of the lines of the spectrum of Gd^{+++} in the crystal $GdCl_3 \cdot 6H_2O$ to definite energy levels. These levels have been fixed by studying the spectrum under various conditions, namely, observing how the lines shift their position with the temperature, observing their polarization, the corresponding lines of the crystal $GdBr_3 \cdot$

[1] Freed and Spedding, Nature **123,** 525 (1929).

Freed and Spedding, Phys. Rev. **34,** 945 (1929).

$6H_2O$, and the behavior of the spectrum in a magnetic field.

The lines that are decomposed by a relatively weak magnetic field invariably break up in two components which are equal in intensity and are symmetrically displaced from the position of the original line. However, dissymmetries occur with stronger fields when the levels produced by the magnetic field approach each other. The dissymmetry in the intensities is especially pronounced. Some of the lines become much stronger while others become weaker, practically vanishing in some cases. A number of the lines coalesce and it has been found impossible to force any crossing with the maximum field at our disposal.

This work was done with a crystal of $GdCl_3 \cdot 6H_2O$ at room temperature. The dissymmetries would undoubtedly have been different at other temperatures as the intervals between the energy levels are then different[2] and consequently the intervals and the interactions between the magnetic levels would no longer be the same.

SIMON FREED
FRANK H. SPEDDING

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May 17, 1930

[2] Freed and Spedding, Phys. Rev. **34**, 945 (1929).

BOOK REVIEWS

Einführung in die Geophysik, II, Erdmagnetismus und Polarlicht, Wärme—und Temperaturverhältnisse der Obersten Bodenschichten, Luftelektrizität, von A. NIPPOLDT, J. KERRANEN, E. SCHWEIDLER. Pp. 388, figs. 130. Julius Springer, Berlin, 1929. Price RM 35. (bound).

The first part on the earth's magnetism and aurorae and the third part on the electricity of the lower atmosphere treat the subjects in pretty much the same way as most other handbooks have done. Brief and adequate discussions are given of what is known about the permanent magnetic field of the earth and its variations, of magnetic storms, of aurorae, of the earth's electric charge, of the potential gradient, ionization and electric current in the lower atmosphere, and of thunderstorms and their electrical effects. The older theories of the phenomena are well presented with, in some cases, an appraisal of the successes and the shortcomings of the theories. The high atmosphere is hardly touched upon, there is almost no mention of wireless wave phenomena. The second part deals in detail with the temperature of the upper few feet of the surface of the land. Temperatures of the soil and of snow are given at various latitudes, on mountains, etc., for various hours of the day and seasons of the year. Some of the results are interpreted with the aid of the mathematics of heat conduction theory.

E. O. HULBURT.

Einführung in die Geophysik, III, Dynamische Ozeanographie, von A. DEFANT. Pp. 222, figs. 87. Julius Springer, Berlin, 1929. Price RM 19.80 (bound).

"Distilled by the sun, kneaded by the moon," swept by the winds, the sea swirls, upwells and drifts in great streams and small eddies. The investigation, both experimental and theoretical, of these movements and of the causes which produce them, that is dynamical oceanography. Hydrodynamics as developed by Lamb dealt for the most part with homogeneous fluids. It was V. Bjerkness, perhap, who laid the theoretical foundation of dynamical oceanography in his papers on the dynamics of heterogeneous fluids.

In the volume under review are chapters on the statics and kinematics of the sea, the general dynamics of ocean currents, stationary currents in a stratified ocean, convection currents, ocean circulation, waves ands tides. A satisfying glimpse is given of the facts gathered by many expeditions on the sea. The mathematics are simple and are applied directly to the analysis of the water movements. Original references are given throughout. One could wish for an English translation of the treatise, for the subject deserves a wider attention in this country than it has received.

E. O. HULBURT

Traité de Polarimetrie. GEORGES BRUHAT. Pp. xvi+448, 250 figs. Editions de la Revue d'Optique théoretique et Instrumentale, Paris, 1930. Price, 65 francs.

The volume is limited to the study of the phenomena of rotatory polarization and the apparatus which serves to measure it. The first part of the book contains detailed discussion of apparatus and technique. The second part is on the phenomena of natural rotation, magnetic rotation, and dispersion of rotation, including circular dichroism in the regions of absorption. This is a very useful handbook for all who have occasion to use the polariscope, whether for chemical analysis, or for the study of the phenomena of rotatory dispersion, circular dichroism, or magneto-optic rotation. The literature is made readily referable by the 882 references. The printing is good, but the binding is poor.

J. VALASEK

The Use of the Microscope. JOHN BELLING. Pp. xi+315, 28 figs. McGraw-Hill Book Company, New York, 1930. Price $4.00.

The many common imperfections of microscope images are described, their causes are given, and the adjustment for optimum high-power microscopy are discussed. The intro-

ductory chapter is planned so that it summarizes the entire text in a form convenient for reference. At the end of the text is a list of 200 review questions and a glossary of microscope terms. Users of microscopes will find many useful suggestions in this volume.

J. VALASEK

Wien-Harms Handbuch der Experimental Physik. Vol. X. G. HOFFMAN—**Das Elektrostatische Feld.** W. O. SCHUMANN—**Hochspannungstechnik.** Akdemische Verlagsgesellschaft m.b.H. Leipzig 1930. Price RM 55 (bound).

G. HOFFMANN. *Das Elektrostatische Feld.* Pp. 345.

Standard texts on electricity and magnetism consider electrostatics as an excuse for the introduction of some of the methods of mathematical physics. As a result little space is ordinarily devoted to the experimental side of the subject. It is very refreshing to see in the present volume a detailed and adequate presentation of the many interesting phenomena connected with static electric fields and of the experimental methods employed in their study. A concise introduction including historical references, definitions of quantities and units, and the most important formulae for capacities constitutes the first section. This is followed by a description and by the theory of instruments. Among these the electrometer is treated in particular detail with definite information concerning the sensitivity and performance of various types. A chapter is devoted to methods of measurement. A general survey of the data on properties of dielectrics is accompanied by a brief description of the current theories and a discussion of the experimental methods used. The experimental facts about the temperature dependence of the dielectric constant and the results of the theory, phenomena of dielectric absorption, volta effect, pyro- and piezo-electricity, conduction through dielectrics are brought up to date.

W. O. SCHUMANN. *Hochspannungstechnik.* Pp. 199.

Essentially a survey of the main points in high voltage engineering. Few books on this subject being available at present this is a very welcome section of the Handbuch. It is of particular interest to see the methods of German engineering practice. On account of the rapid development which took place since the completion of the manuscript much of the recent work has been referred to only in bibliographical addenda, and the volume is therefore already somewhat out of date. The presentation of the older developments is however very clear and contains the essential features of high voltage high power engineering. It is especially pleasing to see a discussion of the theory of dielectric breakdown both from the point of view of physics and of practical electrical engineering.

Both sections are very well illustrated with photographs and diagrams. The index is good and even the spelling of American names is almost correct.

G. BREIT

The Physics and Chemistry of Surfaces. NEIL KENSINGTON ADAM. Pp. 332+x. Figs. 45 Oxford University Press, 114 5th Ave., New York, 1930. Price, bound, $6.00.

For some time, surface tension has been considered as one of the most classical, and accordingly for many most uninteresting parts of physics. Now this field has, thanks mainly to the author of the above book, to Harkins and Langmuir, and to the investigations of heterogenous catalysis, developed into a flourishing branch which gives us many new results, up to now mostly concerning the properties of organic molecules and of crystal surfaces. This book is a very good account of this development, written with an eye on the chemist—even the industrial chemist.

Starting with a short chapter on definitions, it deals in the second chapter with films of insoluble substances. Adam distinguishes four types corresponding to two-dimensional crystals, liquids, compressed gases (the latter two are not sharply separated) and rarefied gases. In the solid films, long chain compounds have their active groups immerged in water while the long chains stand out, closely packed, similar to the arrangement in bulk crystals (Chapter III). In the gaseous films, the molecules seem to lie flat.

The next chapter deals with films of soluble substances and contains an interesting account of the nature of soap films.

Then follows a chapter (V) on the result of surface tension measurements, while a critical survey of the experimental methods is given in chapter IX with sufficient detail for the actual

performance of the experiments and their evaluation. This detailed description occurs also in other chapters and should be very valuable to non-specialists who want to use surface tension measurements. An attempt of a kinetic explanation of Eötvös' rule seems to be at least incomplete because it does not consider the fact that surface tension is only due to the *deviations* from the conditions in the interior.

The sixth chapter describes the behavior of an interface liquid-solid ("wetting"), followed by a chapter on lubrication. Both of these chapters show interestingly, how very practical questions can be better understood with increasing knowledge of molecular properties. Besides the technical problems mentioned above, Adam touches cleaning and dyeing, flotation of ores and (as already in chapter IV) emulsification and the influence of films thereon.

The eighth chapter, on adsorption on solids and its connection with chemical reactions and catalysis, can of necessity contain only a selection of topics. It starts out with the "sensitive patches" of Langmuir and Taylor, the marked increase in activity by mixing catalysts, and the methods for measuring the "microscopic surface" of a solid. Next the work of Langmuir on the theory of absorption and the behavior of gas films, which has already become classical in the good sense, is discussed, followed by selected organic reactions catalysed by metals. Then comes the discussion of charcoal and a little later some very interesting work on the catalytic properties of bacteria. The importance of adsorbed anions on the photosensibility of silver bromide is then discussed. One wonders at the absence of a reference to the pioneer work of Fajans and his school. Finally, the theoretical calculation of surface tension in salts is discussed.

K. F. HERZFELD

Dipolmoment und Chemische Struktur. Edited by P. P. DEBYE. Leipziger Vorträge 1929. Pp. 134+viii, 35 figs. S. Hirzel, Leipzig, 1929. Price Rm 9.

Elektrische Dipolmomente von Molekülen. I. ESTERMANN. Pp. 49, 20 figures, 7 tables. Part of Band VIII, Ergebnisse der exakten Naturwissenschaften, Julius Springer, Berlin, 1929.

Dipolmoment und Molekularstruktur. H. SACK. Pp. 60. 8 figures, 19 tables. Part of Band VIII, Ergebnisse der exakten Naturwissenschaften, Julius Springer, Berlin, 1929.

The first of the three titles reviewed contains lectures given at a Symposium on the connection between the dipolemoment and the chemical structure of molecules, held at the University of Leipzig in the summer of 1929, the two others are articles on the same subject from Volume 8 of Ergebnisse der exakten Naturwissenschaften and can not be purchased separately.

The determination of dipolemoments can be carried out in different ways: (a) By determining the temperature change of the dielectric constant ϵ in the gaseous state, which follows rigorously Debye's formula, if the exact equation of state is used in evaluating (R. Sänger, Zurich), (b) By investigating the deflection of a molecular ray, which is broadened if dipoles are present (I. Estermann, Hamburg).

In this way it is proved that pentaerythrite $C(CH_2OH)_4$ as gas has a moment and therefore the groups CH_2OH are not arranged in a regular tetraeder. (c) By investigating dilute solutions, where all associated molecules are broken up. Following ϵ to higher concentrations and at different temperatures, one can draw conclusions concerning the degree of association and compare them with vapor pressure and viscosity (I. Errera, Brussels).

(d) By subtracting the effects of electronic and ionic (or atomic) polarization from the total polarization (L. Ebert, Würzburg). The former can be determined from measurements of solids sufficiently far from the melting point, the electronic contribution also from the refractive index. To see how large the ionic polarization (displacement of the ions as a whole) is, Errera investigates salt crystals, while K. Hojendahl (Kopenhagen) uses the theory of Born-Landé concerning the forces in the crystal.

The results (Estermann, Errera, Sack, Ebert) show that one can with fair accuracy ascribe definite dipole moments to certain groups in organic compounds and that the resultant moment of a molecule with more than one of these groups can approximately be calculated as a result of a vectorial addition of the moments of each group as predicted by J. J. Thomson. It seems very probable from the results that the benzene ring is flat. The situation is more complicated in the case of groups like C-O-H where the valence bonds form an angle. Here the possibility of rotation of the dipole (lying along OH) around the C-O bond arises. Ebert dis-

cusses in much detail the transition between oscillation and free rotation as well as the question of an influence of the temperature on the apparent value of the dipole.

F. Hund (Leipzig) explains the results of the new quantum mechanics concerning the shapes of simple inorganic molecules.

K. L. Wolf (Karlsruhe) treats two auxiliary methods for solving doubts, which might occur in the interpretation of dipole measurements. These methods are first an observation of the Kerr effect and the depolarisation of scattered light, which are both connected with the unsymmetry of the molecule, and secondly the measurement of the shift of absorption bands for different compounds.

Finally W. Hückel (Freiburg) discusses the influence of the dipole on reaction velocities, especially in so far as there is a connection between the dipole moment and the heat of dissociation or activation of one of the parts of the dipole itself or a neighboring dipole.

K. F. HERZFELD

ERRATUM

AMERICAN PHYSICAL SOCIETY

PROCEEDINGS OF THE NEW YORK MEETING

Through an oversight the titles of the invited papers presented at the Symposium on photoelectric and thermionic phenomena were omitted from the program of the meeting as printed in the March 15, 1930 issue (Phys. Rev. **35,** 656, 1930). On page 668 the following should be inserted after abstract 45:

SYMPOSIUM ON PHOTOELECTRIC AND THERMIONIC PHENOMENA

46. Photoelectric ionization of gases. F. L. MOHLER, *Bureau of Standards.*

47. Photoelectric multiple ionization by x-rays. F. K. RICHTMYER, *Cornell University.*

48. The quantum theory of the photoelectric and thermionic effects in metals. WILLIAM V. HOUSTON, *California Institute of Technology.*

49. The influence of surface conditions on the photoelectric effect. C. E. MENDENHALL, *University of Wisconsin.*

50. The velocity distribution of x-ray photoelectrons. DR. G. WENTZEL, *University of Zürich.*

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE WASHINGTON MEETING, APRIL 24–26, 1930

The 163rd regular meeting of the American Physical Society was held in Washington, D. C., On Thursday, Friday and Saturday, April 24–26, 1930. The Thursday and Friday sessions were held at the Bureau of Standards in the East Building and the Industrial Building. The Saturday sessions were held at the National Academy of Sciences. The presiding officers were Professor Henry G. Gale, President of the Society, Dr. W. F. G. Swann, Vice-President of the Society, and Professors John T. Tate, Harold W. Webb, and L. P. Sieg. On Thursday afternoon and Friday morning there were sessions devoted to papers on "Applied Physics."

On Friday evening there was a dinner for the members of the Society and their friends in the Gold Room of the Washington Hotel. President Gale presided and the speakers were Professors R. A. Millikan, G. F. Hull, Gregor Wentzel, Karl T. Compton and Doctors W. F. G. Swann and L. W. Nordheim. There were 257 guests at the dinner.

At the regular meeting of the Council held on Friday, April 25, 1930, thirty-five candidates were elected to membership. *Elected to Membership*: William Alter, John C. Batchelor, Ralph D. Bennett, John F. Blackburn, George W. Bloemendal, R. M. Buffington, H. R. Byerlay, Stuart Campbell, Shih-Chang Chen, Frank Coleman, T. C. Hardy, R. C. Hartsough, Curtiss R. Haupt, James A. Hootman, Frederick L. Hunter Jr., Franklin S. Irby, Hubert M. James, Carl Kaplan, Horace H. Lagerpusch, S. Lehrman, Leon B. Linford, Ellice McDonald, R. F. Morris, S. M. Naudé, Mr. Parker, John R. Patty, Herbert B. Roese, Oscar Siedman, Caspar V. Shapiro, Johannes A. Van den Akker, Claude C. Van Nuys, Bertram E. Warren, Carl J. Wiggers, Hugh C. Wolfe and Henry H. zur Burg.

The regular program of the American Physical Society consisted of 114 papers, numbers 1, 9, 15, 47, 48, 64, 65, 66, 74, 84, 105, 106, 107, 110 and 113 being read by title. The abstracts of the papers are given in the following pages, An **Author Index** will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. Distribution of non-reacting fluids in the gravitational field. MORRIS MUSKAT, *Gulf Research Laboratory Pittsburgh.*—The paper consists essentially of an analysis of the equation given by Lewis and Randall for the distribution of non-reacting ideal fluids in a gravitational field. When the fluids are incompressible a formal solution is obtained, for a mixture of any number of constituents. But it has not been possible to put it into a form convenient for numerical computation. The ratios of the concentrations of any constituent at the top to that

at the bottom of a vertical column of the mixture are given explicitly, both for incompressible and compressible fluids. When all the molar volumes of the various fluids are equal, the equations are solved completely and lead to a *relative* barometric distribution, and in the particular case of ideal gases, to individual barometric distributions. The physical meaning of this is briefly discussed. The case of binary mixtures is treated in detail, and numerical examples are given, first for a mixture of two paraffins, and secondly for a dilute solution of NaCl in water, which is equivalent to an ideal solution of liquids. As is to be expected, the effect is extremely small, and in the first case it is only one tenth as large as is given by a simple barometric fomula.

2. Capillary retention of liquids in assemblages of homogeneous spheres. W. O. SMITH, PAUL D. FOOTE, P. F. BUSANG. *Gulf Research Laboratory, Pittsburgh.*—The pore space is an assemblage of uniform spheres was initially filled with liquid. After very slow drainage the amount of liquid retained by the spheres was experimentally measured. The liquid is retained in the form of rings at the contacts of adjacent spheres. The radii of curvature of the ring surfaces are computed in terms of surface tension, grain radius and pressure drop across the liquid-vapor interface, permitting calculation of the volume retained per sphere contact. The number of contacts per unit volume of spheres is obtained from porosity measurements using the theory developed earlier. (Phys. Rev. **34,** 1271 (1929).) Computed and observed data on the total volume of retained liquid are in agreement.

3. The mechanism of "atomization." R. A. CASTLEMAN, JR., *Bureau of Standards.*—The process of liquid "atomization" is in wide and important commercial use; yet, so far as the writer knows, no adequate explanation of its mechanism has been offered. The fact, however, that the phenomenon can be used with confidence in the design of machine and other details seems to be sufficient indication of a recognized definite physical background. If we assume that a necessary step in "atomization" is the drawing off, from the unatomized liquid, of ligaments of such size that they will eventually draw up into drops of the size observed in the spray, it appears that a satisfactory explanation of the phenomenon can be obtained by combining Rayleigh's theory of jet disintegration with some recent drop size measurements. For analysis shows that the degree of instability of ligaments of the necessary size is so great that direct observation of either the initial disturbances or even of the ligaments themselves seems improbable. The above assumption appears to be reasonable, necessary and sufficient.

4. Wind pressure on cylindrical stacks. H. L. DRYDEN AND G. C. HILL, *Bureau of Standards, Washington, D. C.*—A summary is given of the published model experiments on the wind pressure on cylinders and of some additional experiments (a) on model cylinders in the wind tunnel, (b) on a large cylinder in the natural wind, and (c) on the power plant stack in the natural wind. The object is to provide a basis for estimating the average wind pressure on stacks and other cylindrical structures at known wind speeds. The conclusions are as follows: 1. The wind pressure on a stack at a given wind speed is a function of the ratio of the height of the stack to its diameter and possibly of the roughness of the surface. 2. Model experiments can not be directly utilized because of a large scale effect. 3. Provision for a wind load equivalent to 20 pounds per square foot of projected area at a wind speed of 100 miles per hour is a safe procedure for stacks whose exposed height does not exceed ten times the diameter. 4. The local values of the pressure may require consideration in the design of thin-walled stacks of large diameter.

5. Airfoils of circular-arc section for use at high speeds. L. J. BRIGGS AND H. L. DRYDEN, *Bureau of Standards, Washington, D. C.*—Experiment has shown that the airfoil sections used in the design of airplane propellers change their aerodynamical properties as the relative air speed approaches the speed of sound. The component of the force in the direction of the airstream (the drag) increases more rapidly than the square of the airspeed, and the component normal to the airstream (the lift) less rapidly. In some earlier measurements, an airfoil which was a segment of a circular cylinder was found to give good results. The present measurements were undertaken to survey the field more thoroughly and to investigate the effect of

rounding the sharp edges. The effect of a moderate rounding was found to be small. At speeds above 0.95 of the speed of sound the circular-arc sections are more efficient than the usual types. At low speeds, (0.5 of the speed of sound), the thick circular-arc sections are much less efficient, but the thin circular-arc sections compare more favorably with the usual types. For propellers operating at high tip-speeds it would be advantageous to use circular-arc sections in the outer parts of the blade.

6. Absorption and velocity of high frequency sound in oxygen. W. H. PIELEMEIER, *Pennsylvania State College.*—Deviations of the experimentally determined absorption and velocity values from their theoretical values in air suggest their determination in oxygen and nitrogen at the same frequencies. The acoustic interferometer and torsion vane methods are used. The torsion vane method is the more reliable but the interferometer makes it possible to make simultaneous measurements of absorption and velocity. The theoretical value of K, the absorption constant, is given by the equation, $K=A/\lambda^2$, where A has the value 0.000365 for oxygen at 20°C. The experimental K is defined by the equation, $I=I_0e^{-Kx}$. The frequency variation of the above deviations can readily be shown by comparing the theoretical value of A, 0.000365, with the observed values. At 1215 kilocycles the radiometer method gave 0.00039. With the interferometer 0.00031 was obtained. At 655.5 kilocycles the radiometer and interferometer both gave 0.00055. Dulong's value for V_0, the velocity at 0°C, of audible sound in oxygen, is 317.2 m/sec. At 1215 and at 655.5 kilocycles the values are 317.1 and 317.4 m/sec respectively. The value given by Laplace's formula is 315.0 m/sec.

7. Influence of the walls enclosing a sounding air column upon the tone quality. DAYTON C. MILLER AND JOHN R. MARTIN. *Case School of Applied Science.*—Three organ pipes are provided, the first made of wood which sounds the tone of $G_2=192$. Two other pipes having the same internal dimensions are made of zinc about 0.5 millimeters thick. One of the zinc pipes is surrounded by a zinc case to form a double walled pipe, with spaces two centimeters wide between the walls. These two pipes have the same pitch, giving a tone a little flater than $F_2=173$. When the single walled zinc pipe is blown in the ordinary manner, its sound has the usual tone quality. By touching this pipe on the outside, extraordinary changes in tone quality can be produced with the formation of inharmonic partial tones, the ratios of which are 1:2.06 :2.66. When the double walled pipe has the space between the walls filled with a liquid the pitch is $E_2=153$. If the liquid is allowed to flow out gradually, the tone quality changes conspicuously during the process with the formation of inharmonic partials having the ratios 1:2:2.9. These experiments indicate that the material of which a musical wind instrument is made may have an important effect upon the tone quality.

8. The excitation of overtones of shear vibrations in Y cut quartz plates. J. R. HARRISON, *University of Pittsburgh.*—It is well known that Y cut quartz plates will function as resonators and oscillators with shear vibrations giving rise to transverse waves in the direction of the Y axis. (W. G. Cady, Phys. Rev. **29**, 617, (1927).) Also it is not difficult to excite the odd overtones, i.e., those frequencies which are approximately odd multiples of the fundamental frequency. With a new type of crystal mounting it has been found possible to excite the even overtones also. To excite the second overtone, a three electrode crystal mounting is used. This mounting consists of two flat electrodes covering the two XZ plane surfaces of the plate and also a frame shaped electrode about one-third as thick as the crystal plate. This third electrode fits around the crystal plate like a frame and is symmetrically disposed with respect to the flat electrodes in the XZ planes. The frame shaped electrode allows fields to be applied between it and the electrodes in the XZ planes in opposite directions. To accomplish this, the flat electrodes are connected together serving as one terminal and the frame shaped electrode as the second terminal. By using two flat electrodes and three frame shaped electrodes, the fourth overtone can also be excited. Similarly, mountings can be constructed for exciting the higher overtones.

9. Torsion of rhombic prisms and of cylinders in the elastic and plastic state. JAKOB KUNZ, *University of Illinois.*—The corresponding problems for isotropic bodies are at first

solved by means of the stress function. The new problems are then reduced to the older ones by means of linear transformations of the variables. The plastic flow is then determined for the elliptic cylinder in a closed form, which however could not be found for the plastic rectangular prism.

10. Some applications of the theory of plastic deformations of ductile metals. A. NADAI, *Westinghouse Elect. Mfg. Co. East Pittsburgh.* (*Introduced by S. M. Kintner*).—A brief account will be given of the principal conditions which are available to express the equilibrium of stress in the plastic state of ductile metals. These conditions will be discussed for the case of rotationary symmetry in a plastic body. As an example several cases of plastic flow in a thick walled cylinder subjected to high internal pressure with and without longitudinal expansion will be treated. The distribution of stress during yielding is given for a long cylinder and for a flat ring both subjected to radial pressure. How yielding and the plastic deformation spread through the walls of the cylinder will be shown.

11. The flarimeter: a clinical instrument for testing circulatory fitness. P. V. WELLS, *Medical Department, The Prudential Insurance Company of America.*—Forced expiration at constant lung pressure of 20 mm provides the most convenient means of placing the circulatory system under standard load. The response in systolic blood pressure is maximum at rates about 36 cc/sec. Among normals, the blow should exceed 50 seconds; its decrease measures shortness of breath, the leading symptom of an impaired heart muscle. The blood pressure normally rises 20 mm in 45 sec, 40 mm before the impulse to breathe stops the blow. The Flarimeter is a simple durable, reproducible, inexpensive, portable instrument designed to enable an individual to perform such a standard test. A 200 cc/sec orifice is also provided, its length of blow giving an accurate measure of vital capacity (the volume of a maximum single expiration). Some investigators have believed the vital capacity to be a measure of shortness of breath because it is so reduced in heart disease. But after exercise the vital capacity is not reduced, while the small orifice blow is shortened to a third of normal length, showing that it is a much better measure of shortness of breath.

12. Suggested explanation of Michelson-Morley-Miller experiment. N. GALLI-SHOHAT, *Mount Holyoke College.*—The complete theory of Michelson-Morley-Miller experiment leads to two effects: one due to the phase difference, another to the "rotation" of the waves produced by reflections from the moving mirrors. P. Epstein has given an estimation of this last effect and has found it too small to be discovered. However, his estimation was based on the orbital velocity of the earth, 30 km/sec, while the velocity of the solar system in space is much greater. Thus if one makes an estimation of the "rotational" effect for $v=300$ km/sec. one gets a displacement about 0.2 fringes in agreement with what Professor Miller has observed under the conditions of his experiment. This suggests the following assumptions: *Phase effect is fully compensated (Lorentz contraction); effect actually discovered by Miller is a rotational effect* due to the aberration X' observed by Esclangon and discussed in the previous paper. Rotational effect is assumed to be proportional to the horizontal component of X', being $\beta^2 l \cos\theta$ $(\sin^2\theta - \cos^2(v_1\ z))^{1/2} = [\theta = (v_1 l),\ Z\text{-zenith}]$. The curves, representing the variation of the azimuth of the maximum effect and its magnitude, computed for Mt. Wilson, using the apex-declination 68° agrees with the curves given by Miller; the agreement being most striking for the data 1925.

13. The magnetic moment of the lithium nucleus. S. GOUDSMIT AND L. A. YOUNG. *University of Michigan.*—The hyperfine structure observed by Schüler in ionized lithium is of the same order of magnitude as the multiplets in that spectrum. This has led to the belief that the magnetic moment of the nucleus must be of the same order of magnitude as that of an electron. However, the hyperfine structure is produced by the deeply penetrating $1s$ electron whereas the multiplet separation is due to the outside $2p$ electron. These two should thus not be compared and indeed rough calculations show that a nuclear magnetic moment of only a few proton units is sufficient to account for the hyperfine structure. The considerations of H. E. White on lithium as well as other hyperfine structures (Phys. Rev. **35**, 441 (1930)) are

incorrect since he erroneously compares them with singlet-triplet and other "Austausch" separations. His error is caused by a misinterpretation and a too literal application of the vector model.

14. Possibility of bringing mean life directly into Schroedinger equation for the hydrogen atom. A. BRAMLEY AND ALLEN C. G. MITCHELL, *Bartol Research Foundation.*—The possibility of bringing an expression for the mean life of an atom in a given state directly into the wave equation for the hydrogen atom with relative motion of the nucleus, has been investigated. A solution for the electron and proton in their mutual coulomb field has been found which contains a damping term β occurring in the time factor of the equation for

$$\Psi_m{}^t = \Psi_m \exp(2\pi i/h)(E_m + i\beta)t.$$

The value of the constant β is determined from the condition, that if the atom is in the state designated by eigenwert E_m for the electron at time $t=0$, then the probability of making a transition to any other state in all time is unity; or expressed analytically

$$\sum_n \alpha_{mn} \int M_{mn} dt = 1$$

where M_{mn} is the matrix moment of the transition. This leads to a value of β_m (reciprocal of mean life) which is proportional to $[\sum_n \{\int x u_m u_n^* dx dy dz\}]^2$. This expression is similar to the expression derived by Sagiura from the Correspondence Principle for the value of the mean life.

15. Life and radius of the metastable mercury atom. M. L. POOL. *Ohio State University.*—The experimental arrangement described by the writer (Phys. Rev. **33,** 22, (1929)) has been altered in order to lend itself more easily to mathematical treatment. A quartz resonance cell containing mercury vapor at 25°C is placed between two high speed disks which interrupt the total radiation from two symmetrically placed water-cooled and magnetically controlled quartz mercury arcs. A few millimeters of purified nitrogen and a trace of water vapor is admitted into the resonance cell and slowly moved over hot copper and copper oxide. The life of the 2^3P_0 state is measured by the rate of decrease of the absorption of 4047 with increasing time-wait after optical excitation of the mercury vapor. Extrapolation to zero nitrogen pressure gives a natural life of about 2×10^{-3} sec. Admixtures of argon at low nitrogen pressures prevented rapid diffusion of the metastable atoms to the walls of the tube. A treatment of the life-time similar to that outlined by Zemansky (Phys. Rev. **34,** 213 (1929)) gives the radius of the metastable atom to be 2.4 to 3.0×10^{-8} cm depending on the pressure of the admixed nitrogen.

16. Interval rule for sp, sd, sf configurations. E. U. CONDON AND G. H. SHORTLEY, *University of Minnesota.*—A systematic comparison of the known data on the singlets and triplets arising from *sp, sd, sf* configurations with the theory of Houston (Phys. Rev. **33,** 297 (1929)) shows that the theory gives a good account of the deviations from the Landé interval rule which accompany departure from Russell-Saunders coupling. There are numerous significant discrepancies, however. Writing ${}^1L_l$ and ${}^3L_{l+1}$, ${}^3L_l$ ${}^3L_{l-1}$ with $L=P, D, F$, when $l=1, 2, 3$ for the term values, we plot as abscissas $({}^3L_{l-1}-{}^3L_{l+1})/|{}^3L_l-{}^1L_l|$ and $({}^3L_{l-1}-{}^3L_l)/({}^3L_l-{}^3L_{l+1})$ as ordinate if $({}^3L_l-{}^1L_l)$ is positive, otherwise the reciprocal of this quantity. Houston's equations (12) give functional relations between these interval ratios which are compared with the experimental values.

17. The resonance of $(B-A)$ bands of the hydrogen molecule. HUGH H. HYMAN, *Union College.*—Photographs of the extreme ultraviolet spectrum (λ 1100A to λ1640A) have been taken, using a vacuum spectrograph made available to the author at the University of California. A three inch grating, 15000 lines per inch with a three meter focal length, was used, giving a resolving power of 0.1A and a dispersion of 2.76A per millimeter in the second order. The fine structure of sixty eight bands of the first resonance (B−A) system has been studied. The moment of inertia of the normal (A) state is found to be 0.4673×10^{-40} g.cm², the nuclear

separation, 0.7500×10^{-8} cm. In the first excited (B) state the moment of inertia is given as 1.4225 g.cm^2 and the nuclear separation as $1.308_4\times10^{-8}$ cm. Resulting constants leave no doubt but that the B state is also the lower state of bands found in the visible and studied by Richardson and Davidson. The proof of the connection between the ultraviolet system and the visible system leads to the conclusion reached by Birge that the ionization potential of the hydrogen molecule is 15.34 volts to within a few hundredths of a volt.

18. Regularities in the spectra of lutecium. WILLIAM F. MEGGERS AND BOURDON F. SCRIBNER, *Bureau of Standards.*—A study of the arc and spark spectra of lutecium (71 Lu) resulted in the separation of the lines into 3 distinct classes. (1) those characterizing neutral atoms, constituting the Lu_I spectrum; (2) those due to singly ionized atoms, the Lu_{II} spectrum and (3) a small number of lines ascribable to doubly ionized atoms, the Lu_{III} spectrum. Regularities have been discovered in each of these spectra. The normal state of neutral Lu atoms is represented by a ^2D spectral term arising from the electron configuration (s^2d); its levels are separated by 1993.9 wave-numbers. The normal state of Lu^+ atoms is described by $^1S(ss)$, and metastable terms ^1D, ^3D (ds), $^3F'(dd)$ have also been established. The relative values are as follows:

$$^1S = 0.0, \quad ^3D_1 = 11796.1, \quad ^3D_2 = 12435.2, \quad ^3D_3 = 14199.0,$$

$$^1D_2 = 17332.5, \quad ^3F_2' = 29406.7, \quad ^3F_3' = 30889.1, \quad ^3F_4' = 32503.7.$$

A $^2S(s)$ term describes the normal state of Lu^{++} atoms; a ^2D (d) term has levels at 6304.3 and 8648.1. There is no evidence that f-electrons play any part in the production of the spectra; it is concluded that the fourteen f-electrons in Lu form a closed shell of considerable stability.

19. The spark spectrum of cobalt (Co II). J. H. FINDLAY, *Princeton University.*—A further examination of the Co II spectrum, based on the previous work of Meggers (Journ. Wash. Ac. Sci. **18**, No. 12, 1928), has been made. A magnetic analysis shows that Meggers' classification of the terms $d^7p\,^5F^0$, $^5D^0$ should be interchanged, except for the term $^5F_5{}^0$. Since Meggers' results were obtained from intensity rules, the author's $^5F\,^5F^0$ and $^5F\,^5D^0$ multiplets show irregular intensities. The strongest lines in these multiplets are, respectively, ^5F_n $^5F_{n-1}$ and ^5F_n $^5D_n{}^0$. The magnetic analysis also shows that Meggers' terms ^3D should be $d^7s\,^5P$ and that his $^3P^0$, $^3D^0$, and $^3F^0$ should be partly $d^7p\,^5P^0$ and $^5D^0$. In addition, the terms $d^7s\,^3F$, $d^7p\,^3D^0$, $^3F^0$, $^3G^0$, $^5S^0$, and the lowest terms $d^8\,^3F$ have been found. The location of the second member of the $d^7s\,^5F^0F$ series gives an I. P. of 16.9 volts from d^7s to d^7 and 17.3 volts from d^8 to d^7, in practically exact agreement with the predictions of Dr. H. N. Russell.

20. A surplus level in the arc spectrum of palladium. A. G. SHENSTONE, *Princeton University.*—The spectrum Pd I has been so thoroughly analyzed that the positions of all the structures to be expected are known. One even level, k_1 of Bechert and Catalan, is apparently not explainable in terms of the Hund theory unless it is a hyperfine structure component of $d^95d\,^3P_1$. That explanation is extremely improbable since (1) it makes the hyperfine structure greater than the fine structure and (2) no other levels are known to have structure. The lines due to k_1 are peculiar in being the only diffuse lines in Meggers' list which extends from λ4500 to λ9200.

21. Spectra of gases lighted with strong discharges. E. O. HULBURT, *Naval Research Laboratory.*—Spectra of condensed discharges through hydrogen at pressures up to several cms of mercury showed, as usual, the Balmer lines merging into the continuous spectrum. With increasing strength of the discharge the Balmer lines widened, the higher members of the series disappeared and the continuous spectrum became more intense, until with 1 microfarad at 15 kilovolts (the method of J. A. Anderson, Astrophys. J. **51**, 37 (1920)) there were no Balmer lines left at all, only the continuous spectrum and some absorption lines due to aluminum from the electrodes, etc. Helium, oxygen and nitrogen exhibited similar changes, i.e., with increasing intensity of discharge in helium the lines gave way to a continuous spectrum, and in oxygen and nitrogen the molecular bands gave way to spark lines and these in turn to a continuous spectrum. The continuous spectra from all the gases were alike. The intensity

distribution across the continuous spectrum was rather even and hardly that of a black body. In the strong discharges the external characteristics of the atoms were pretty well effaced and the conditions approached those in the interior of a star.

22. Excitation processes in the hollow cathode discharge. R. A. SAWYER, *University of Michigan.*—The negative glow inside a hollow cathode in a rare gas discharge has often been used to excite metallic spark spectra. The excitation is largely due to collisions of the second kind between gas and metal atoms and ions. The exact processes may be inferred from the observed highest term excited and from maxima or abnormal intensities in the metallic spectrum. The available data have been examined. In general only those processes occur in which the metal can be excited to some term in the spark spectrum with gain or loss of only a small a amount of kinetic energy to balance the reaction equation. If the metal has a low vapor pressure or sputters poorly cathodically the metal atoms in the normal state or a low metastable state if any will be excited by collisions with gas ions and metastable atoms. If the metal has a high vapor pressure metal ions will enter the reactions. In intermediate cases metal ions may or may not enter depending on conditions. The limit of excitation is fixed by the possible reaction yielding the greatest energy; the other possible reactions may produce maxima in the spectra.

23. Collisions of the second kind and their effect on the field in the positive column of a glow discharge in mixtures of the rare gases and mercury vapor. O. S. DUFFENDACK AND L. B. HEADRICK, *University of Michigan.*—Measurements were made of the electric field in the positive column in mixtures of helium-neon, helium-argon, neon-argon, in all proportions and mixtures of each of these gases with mercury vapor. Spectrograms were taken of the radiation from the positive column for each of these mixtures. The electrical and spectral characteristics of the positive column in mixtures of monatomic gases can be explained in terms of collisions of the second kind between the metastable atoms or the ions of one gas and the neutral or the metastable atoms of the other. The necessary condition for a large effect to be produced by a small amount of one gas added to another is that there exists a close resonance between the metastable states of the main gas and the ionized or excited states of the added gas. The introduction of only 0.15% argon into neon produced a marked increase in the electric field and the spectrum emitted changed completely from neon I to argon I, while the addition of 10% neon to argon had practically no effect.

24. Secondary emission from nickel in a neon discharge. W. UYTERHOEVEN AND M. C. HARRINGTON, *Princeton University.*—Continuing experiments on the secondary emission from a negatively charged metal collector placed in a neon discharge (Science **70**, 586, 1929) we obtained additional evidence of a secondary electron current amounting to about 40% of the total current. With the experimental arrangement described before, a perforated collector with a Faraday box behind it, (Phys. Rev. **35**, 438, 1930) an estimate can be made of the electron emission due to metastable atoms. This is found to be much more important than the part due to ion impact, namely about 30 to 35% of the total current. When this is deducted from the total secondary emission, values for the number of electrons liberated per incoming positive ion can be estimated. This comes out of the same order of magnitude (10%) as the values determined directly by Penning (Physica **8**, 13, 1928).

25. The effect of intense electric fields on the photoelectric behavior of thin potassium films. ERNEST O. LAWRENCE AND LEON B. LINFORD, *University of California.*—Photoelectric thresholds of thin films of potassium on tungsten were observed at 5620A with fields drawing the electrons from the surface of 260 volts/cm. Increasing the applied fields shifted thresholds towards the red, for example, to 5880A by a field of 26,000 volts/cm. It is calculated from the data that at distances between $7(10^{-7})$ cm and $12(10^{-7})$ cm of such surfaces the field is entirely the Schottky image field while at greater distances the field exceeds the image field, indicating patched surfaces. Films of potassium on thick layers of oxygen on tungsten show no dependence on fields, indicating either that ion layers exist more than 300 atom diameters from the metal surface which produce fields greater than the Schottky field or that such surfaces are rough. Poor current saturation indicates the latter as more probable. Potassium on a thin oxide layer

has a threshold farthest to the red and exhibits dependence on applied fields assignable to image forces alone. Wentzel's wave mechanics theory of the photoelectric effect is verified in the respects that the whole photoelectric sensitivity curve shifts with the threshold and that the maximum sensitivity occurs at a frequency 3/2 the threshold frequency.

26. A representation of the dynamic properties of molecules by mechanical models. C. F. KETTERING, L. W. SHUTTS AND D. H. ANDREWS, *General Motors Corporation.*—Mechanical models have been constructed to represent the dynamical systems found in the molecule. Assuming that the intramolecular forces lie along lines associated with the chemical bonds and that for small vibrations they obey Hook's law and have the mechanical character of spiral springs, it is possible to get a picture of the forces and masses which can be represented on a large scale by steel balls and spiral springs. Models have been constructed for some of the simpler nonpolar molecules. They are found to have characteristic frequencies which correspond very closely to the frequencies observed in the Raman spectra and it is possible by this means to identify the Raman lines with definite types of motion of particular atoms in the molecule. This substantiates the view that Raman lines correspond very closely to characteristic fundamental molecular frequencies.

27. The fluorescence spectrum of benzene. F. ALMASY, *University of Zurich,* AND C. V. SHAPIRO, *Cornell University. (Introduced by R. C. Gibbs).*—Using an improved technique, the fluorescence spectrum of benzene, excited by the radiation from a quartz Hg arc, has been photographed with a Hilger E_1 spectrograph, whose dispersion in the region under investigation is 3A per mm. Wave-length measurements were made from an Fe spark comparison spectrum. The data so obtained are in excellent accord with those for the absorption spectrum in the range over which the two overlap. An energy level diagram is proposed which accounts for the majority of the bands on the assumption that the electronic origin of the system lies at 37489 cm^{-1} (see following abstract). The vibrational frequencies are 923 cm^{-1} for the excited state and 998 and 160 cm^{-1} for the normal state.

28. Electronic transitions in the spectra of benzene. C. V. SHAPIRO, R. C. GIBBS AND J. R. JOHNSON, *Cornell University.*—A review of the available data on the absorption and emission spectra of benzene, together with new data on the absorption of the vapor at higher concentrations, leads to the definite conclusion that only two electronic transitions need be assumed in setting up an adequate energy level scheme, as opposed to the recent suggestions of 5 and 3 respectively, by Austin and Black, (Phys. Rev. **35**, 457 (1930)) and by Black, (Nature, **125**, 274 (1930)). These two values are 37489 and 38612 cm^{-1} and are identical with those previously assigned by Henri, Structure des Molecules, Paris, (1925), pp. 109, 110. The observed fluorescence spectrum is confined solely to the first of these two systems, while the absorption spectrum is distributed between the two, though showing a much greater intensity in the second. The Tesla luminescence spectrum is very similar to the fluorescence spectrum, except that a few bands corresponding to the most intense of the absorption bands of the second system, do appear.

29. Polarization of sensitized fluorescence. ALLAN C. G. MITCHELL, *Bartol Research Foundation.*—The question of whether or not angular momentum of optical electrons is conserved on a collision of the second kind between an excited mercury atom and a cadmium atom has been investigated. It is well known that under certain conditions mercury resonance radiation is almost completely polarized. It is also known that an excited mercury atom can give its energy to a cadmium atom causing this atom to emit its resonance line λ 3261. In this experiment a mixture of Hg and Cd vapors was radiated by light from a quartz-mercury arc (giving the unreversed 2537A Hg line). The electric vectors of the exciting light were in the X-Z plane. The Hg-Cd mixture was in a magnetic field (300 gauss) directed in the y direction. The fluorescence from the mixture was observed through a Savart Plate and Nicols prism in the X direction. Under the conditions of the experiment (low pressures of Cd and Hg vapors) the fluorescent light consisted of the 2537A line of Hg and the 3261A line of Cd. The Cd line was unpolarized whereas the Hg line was polarized. Had the polarization been carried over on collision one would have expected the Cd line to be polarized in the same direction as the Hg line.

30. The chemiluminescence of metallic sodium. JAY W. WOODROW AND R. M. BOWIE, *Iowa State College.*—It has been known for a long time that metallic sodium and potassium will give off a faint bluish glow when a fresh surface is exposed to the air. This has been attributed to direct oxidation upon contact with the oxygen in the air. A careful check of this effect, however, has shown that it is mostly, if not entirely, due to the water-vapor present. A special apparatus was constructed by means of which it was possible to feed into a gas chamber a fine thread of metallic sodium which always had a fresh surface. When carbon-dioxide or oxygen which had been bubbled through water was passed into this chamber, the sodium thread glowed quite brightly. The effect appeared to be as prominent for the moist carbon-dioxide as for the moist oxygen. On the other hand neither dry oxygen nor dry carbon-dioxide gave an effect which could be detected by the eye even after a half hour in absolute darkness, while at the same time a freshly cut surface of sodium, used as a check, was clearly visible in open air.

31. An electrical method of determining the gelation temperature of starch. E. C. MCCRACKEN, *Iowa State College.*—During an investigation of the electrical properties of the potato, it was observed that there was a discontinuity in the resistance-temperature curve. As the potato was heated by an electric current passing directly through it, a sudden decrease in the resistance took place at a temperature between 87° and 88°C. This effect was undoubtedly due to a disruption of the starch grains. Chapman and others have concluded from measurements with the viscometer that this phenomenon takes place at a temperature near 90°C. The electrical resistance method has been found to be quicker, simpler and more accurate for determining this gelation temperature than that in which the viscometer is used.

32. Absorption of ultraviolet light by lacquer films. W. P. DAVEY AND D. C. DUNCAN, *The Pennsylvania State College and Hercules Powder Co.*—Absorption tests on a series of nitrocotton films, film solutions and their various individual ingredients yielded the following results: None of the films showed selective absorption. They were completely opaque to radiation of wave-length less than about 3300A. Absorption decreased markedly with increasing wave-length, becoming inappreciable for wave-lengths greater than 4000A. The absorption was found to be quite independent of viscosity, nitrogen content and such plasticizers as were used. The limitation of transmission to wave-lengths greater than 3300A was found to be due to ester gum, a constituent common to all of the films. The nitrocotton constituent was quite transparent to wave-lengths greater than 3000A. Similarly, tests on a series of cellulose acetate films, film solutions and their various individual ingredients yielded no evidence of selective absorption. In this series there was no close correlation between the absorption characteristics of the dried films and the solutions from which the films were made. This was found to be due to the fact that the absorption of the solvents present masked that of the other ingredients. Absorption of solvent-free cellulose acetate films for wave-lengths greater than 2900A was found to be due to the particular plasticizer used.

33. Transmission of ultraviolet radiation by lake water. CHARLES D. HODGMAN, *Case School of Applied Science.*—Pure water, relatively transparent to the ultraviolet, is rendered less so by the presence of small quantities of dissolved salts and organic materials such as occur in natural river and lake waters. The extent to which ultraviolet radiation, either from the sun or from artificial sources, penetrates such media is of interest for many reasons. A series of measures of the transmission of unfiltered water from Lake Erie, made by the sector photometer and quartz spectrograph for a thickness of 2 cm shows a relatively low transmission ranging from about 74 percent at 0.40μ to 12 percent at 0.22μ. Determinations are in progress for water from the same source after filtration and as taken from the city water supply as well as from other sources.

34. Measurement of intensity of helium lines with voltage using a photoelectric device. JOSEPH RAZEK AND PETER J. MULDER, *University of Pennsylvania.*—The variation of intensity with exciting voltage for the lines 6678, 5876, 5016, 4713, 4471, of the helium arc spectrum has been measured using the automatic photoelectric spectrophotometer described by Mulder and Razek before the Ithaca Meeting of the Optical Society of America in Oct. 1929. It was found

the results on 6678(1^1P-2^1D), 5878(1^3P-2^3D), 5016(1^1S-2^1P), 4471(1^3P-3^3D) were generally smooth curves, differing somewhat from the results of Hughes and Lowe, (Proc. Royal Soc. **A104,** 1923 Pg. 480) whereas 4713(1^3P-3^3S) shows undoubted maxima near the critical exciting potentials consistent with the results reported by Cornog, (Phys. Rev. **32,** 746–752 (1928)). The radiation was developed in a spherical equipotential space 20 cm in diameter, formed of a hollow copper ball. The equipotential cathode and grid from a commercial power tube formed the internal structure, the sphere itself being the anode. The filament, grid and outer sphere were connected to the positive of a battery, with the cathode as the only part inside the sphere at a lower potential. This resulted in a very uniform potential inside the sphere. Direct light from the cathode was cut out by means of a diaphragm on the window in the sphere through which the light was examined. Arc currents as high as 300 milliamperes were obtained with 50 volts across the tube.

35. Further experiments with an automatic photoelectric spectrophotometer. PETER J. MULDER AND JOSEPH RAZEK, *University of Pennsylvania.*—The automatic photoelectric spectrophotometer described by Razek and Mulder before the Optical Society of America, October 1929, has been satisfactorily applied to a series of problems, some of which are detailed. Certain changes in the instrument made possible operation at about ten times the former sensitivity when desired. In this way differences in very dark samples, having an intrinsic brightness of only a few percent, can be readily shown. By a series of tests on biological pigments, the instrument was shown to be admirably suited for testing any solutions that change color rapidly. Three records were taken on an acid hematin solution in six minutes, showing three different stages in its light transmitting property. Records have also been obtained on a 1% solution of oxyhemoglobin in water, both when fresh and when reduced. One record was obtained showing the oxyhemoglobin in the act of reduction. The effect of surface gloss of the sample was tested and found to be negligibly small. All records mentioned, and various other interesting color analyses will be shown.

36. Pictures in relief made with a large diameter lens. HERBERT E. IVES, *New York City.*—Pictures showing relief through a large range of angles and distances of observation (parallax panoramagrams) have heretofore been made by the use of a moving lens, and an opaque line grating slightly separated from the sensitive plate, both plate and grating also being moved in some schemes. All moving parts may be eliminated if a single stationary large diameter lens is substituted for the small moving lens, and provided (a) the transparency positive is placed in front of the grating instead of behind it, (b) the image is given a single inversion, as by a mirror, (c) a grating is used for viewing which has a slightly greater line spacing than the taking grating. The resulting relief pictures are visible through the angle subtended by the lens from the object. The method has the advantages of simplicity of apparatus and manipulation, and of greatly shortened exposure time.

37. Alloys for vacuum-tight glass-metal joints. BY D. E. OLSHEVSKY, *Yale University.*—Joints between materials possessing different physical properties constitute an essential feature of much apparatus involving high vacuum. A glass-metal solder joint occupies—as far as assembling and disassembling is concerned—a position intermediate between direct metal-glass seal and the classical ground joint. In an attempt to find suitable solders ternary alloys of Pb, Sn and Bi were investigated first and characteristic breakages occurring some time after solidification were found to be due to little hard crystals growing out of the interface and pressing against the surface of glass. Several alloys laying on straight lines $E-$Pb, $E-$Sn and $E-$Bi as well as in the $E-e_1$, $E-e_2$, and $E-e_3$ valleys (Int. Crit. Tables, v. II, p. 418) were investigated by pouring into Pyrex tubing moulds. An alloy lying on the $E-$Pb straight line (Pb 50, Bi 37.5, Sn 12.5) was found to possess small glass cracking tendency. This is attributed to separation of soft Pb crystals on cooling. In agreement with the above, alloys obtained by shifting from the eutectic of Pb–Bi–Sn–Cd on a straight line toward the Pb corner (as Pb 31.1, Sn 12.5, Bi 47, Cd 9.4) were also found to have no tendency to burst glass, even in thin layers between glass and metal. The vacuum-tightness of the alloys is still unsatisfactory and joints must be backed by cement for high vacuum work. The joints proved in actual service to be mechanically strong, rigid, vacuum tight and replacable. Further study is in progress.

38. Studies in contact rectification, II. The cupric sulfide-magnesium junction. MILTON BERGSTEIN, J. F. RINKE, AND C. M. GUTHEIL, *Research Laboratory, P. R. Mallory & Co., Inc.*—The commercial cupric sulfide-magnesium rectifier junction consists of a disk of heat-treated, compressed, cupric sulfide powder contacted with the suitably oxidized face of a magnesium disk. The efficiency of the rectifier unit increases with operating temperature within usual working limits. The phenomenon of "reverse rectification" (i.e. rectification in the direction opposed to normal) is related to the a.c. voltage across the junction. Oscillograms show that there is formation of a film which possesses resistive properties in one direction, that the film may be partially destroyed by continued passage of current in the conductive direction, that application of sufficient voltage in the resistive direction causes re-formation of the film in less than 0.004 sec., that there is no battery effect or thermoelectric effect sufficient to account for rectifying properties, and that formation of the film is probably electrothermic rather than electrolytic in origin.

39. The effect of cyclones and anticyclones upon the intensity of radio signals. R. C. COLWELL, *West Va. University.*—Observations made up by the signal variation of station KDKA at Pittsburgh have shown that the signal intensity increases after nightfall provided there is a low pressure area between Pittsburgh and Morgantown. Hence an increasing intensity after nightfall is an indication of cloudy or stormy weather the next day. An area of high pressure between Pittsburgh and Morgantown will cause the night signal to decrease, so that this type of signal curve indicates fair weather. If the low pressure area passes south of Morgantown, it does not effect the signal. Such a low pressure brings rain with an east wind changing to north and a storm of this kind is unpredictable by observations upon a station to the north of the observer. As with the barometer, the readings indicate weather conditions twenty-four hours in advance.

40. Reflection of radio waves from the surface of the earth. LAL C. VERMAN, *Cornell University.* (*Introduced by E. Merritt.*)—The reflection of an elliptically polarized electromagnetic wave from partially conducting and perfectly conducting surfaces is studied in detail. It is shown that in either case the interference of incident and reflected waves gives rise to a psuedo-stationary wave field above the surface of the reflector. This field is bodily propagated along the horizontal projection of the direction of the incoming wave with a velocity greater than that of light, i.e. $c/\sin\alpha$, where α is the angle of incidence. The resultant electric and magnetic vectors at any given point above the reflector describe two field ellipses lying in two different planes, whose orientation vary with height. This fact is made the bases of experimental measurements.

It is found that the 43 meter wave from WIZ, located in New Brunswick, N. J., holds its polarization and angle of incidence constant during morning hours at Ithaca, N. Y. The rapid fading that accompanies the signal is to be attributed to amplitude fluctuations. Observations on this station are analyzed on the basis of the above theory to obtain the angle of incidence and the polarization of the incoming wave. Polarization is found to be generally elliptical.

41. The x-ray fiber structure of alloys containing precipitated crystals. CHARLES S. BARRETT, *Naval Research Laboratory, Washington, D. C.*—Dahl, Holm, and Masing (Wiss. Veröffentlich. Siemens-Konzern **8,** 154–185, 1929) prepared cold drawn wires of Be in solid solution in Cu which showed [111] and [100] directions along the wire axis. Annealing these at 350° precipitated a compound of CsCl structure with both [110] and [100] directions in the axis of the wire, the first of which is "a typical crystal position for (fibered) body-centered lattices." Their comparison to ordinary body-centered fibering is without significance because the precipitate was absent when the wire was drawn. The preferred orientation of the precipitate is not due to processes of slip in the precipitate itself, but is due to the precipitate forming with definite orientation on certain planes of the solid solution. Young (Proc. Roy. Soc. **A112,** 630, 1926) observed such a relation of orientation in meteorites. Similarly, a solid solution of Ag in Al (21.3% Ag) precipitates on (111) planes, with (00.1) hexagonal close-packed precipitate planes parallel to (111) solid solution planes and with [11.0] and [110] directions in these planes parallel, as determined by an analysis of x-ray diffraction from wires.

42. An x-ray determination of crystal orientation in silver sheet, produced by cold rolling. CLEVELAND B. HOLLABAUGH, *The Pennsylvania State College.* (*Introduced by Wheeler P. Davey.*)—Sheet silver, 99.9%, free from preferred orientation was rolled in 2 1/4 inch rolls and the orientations determined after each pass using the method of Davey, Nitchie and Fuller. (Mines and Met. Tech. Pub. **243,** E, 88.) Two symmetrical orientations were found which were independent of the technique of rolling. To picture the resulting preferred orientation, visualize a face-centered cube, with the cube face parallel to the surface of the sheet and with the face diagonal in the direction of rolling. Using the other face diagonal as an axis, rotate the cube until this diagonal makes an angle of not less than 10°, nor more than 42° with the surface. Allow this cube to be rotated at random about the rolling direction as an axis. Any point in this random rotation is within the preferred ranges, provided the face diagonal is in its range of positions. In one of the preferred orientations the direction of rotation is such as to raise that end of the face diagonal which points to the end of the foil entering the rolls first. The other orientation lowers this end of the face diagonal.

43. Radial-asterism in multi-crystalline materials. C. NUSBAUM, *Case School of Applied Science.*—The phenomenon of radial asterism as seen in a Laue photograph of a distorted single crystal is generally attributed to internal strain, whether the strain is produced by a uniform bending moment, compression or tension. It is thus a suitable means for the detection of the presence of internal strains in multi-crystalline materials. A study has been made of radial asterism in such iron samples when subjected to a variable but uniform bending moment. The results are qualitative in nature but are related to the magnitude of the distortion.

44. An x-ray study of very pure iron. O. L. ROBERTS. *The Pennsylvania State College.*—Iron, from chemically pure ferric nitrate, (Baker's Analyzed), was precipitated as the hydroxide and reduced to the metallic state by oxygen-free, dry hydrogen. The metallic powder was pressed into wire form, sintered and swaged. This should give a strictly carbon-free iron. Spectroscopic tests show that the iron is especially free from these impurities. Diffraction patterns were obtained at various temperatures close to the recalescence temperature so as to find the lowest temperature which would cause the change from the body centered to face centered cubic structure. The whole apparatus, including photographic film, was inclosed in an atmosphere of hydrogen. Grain growth was found to take place to a large extent. Face centered cubic structure exists at 921°C.

45. The effect of an electric field on the x-ray diffraction pattern of a liquid. RONALD L. MCFARLAN, *University of Chicago.*—An investigation is made of the effect produced on the x-ray liquid diffraction pattern by an electric field so designed as to give the Kerr effect for the liquid under examination. The liquid diffraction pattern is obtained by replacing the crystal of a Bragg spectrometer with a cell containing the liquid. The electric field is applied approximately normal to the x-ray beam. Under a potential gradient of 9 kv per cm nitrobenzene shows a 2.3 percent increase in the intensity of the diffraction peak, while for a gradient of 5 kv per cm it shows an 0.8 percent increase. Benzene, which shows no Kerr effect for the type of field used, gives a 0.3 percent decrease in peak intensity, the potential gradient being 9 kv per cm. The probable error in all these cases is 0.3 percent. There is thus indicated a small but detectable tendency of the nitrobenzene molecules toward a definite orientation with respect to the electric field.

46. X-ray diffraction in water 2° to 98° C: The nature of molecular association. G. W. STEWART, *State University of Iowa.*—X-ray diffraction ionization curves of water show (1) the presence of two definite peaks corresponding to the separation of diffraction planes of 3.27A and 2.11A; (2) the practically constant diffraction intensity of one peak over the temperature range, 2° to 98°C as compared with the gradual disappearance of the second peak with increasing temperature; (3) correspondence in angle of diffraction between these peaks and the chief diffraction intensities with ice crystals; and (4) the increase of peak width with increasing temperature with a movement indicating less distance of planes. It is difficult to reconcile these results with what was formerly regarded as the alteration, in complexity of

the water molecule. The simplest explanation emphasized by all the experiments in x-ray diffraction in liquids, is that the so-called molecular complexity is the arrangement of molecules in more or less orderly groups with intermolecular forces of distinct magnitude. With temperature increase the nature of the group changes, one set of planes becoming more poorly defined because of more slippage and less orderly arrangement. The alteration in grouping is also shown by the decrease in distance between planes. The group arrangement (cybotactic condition) describes the nature of what has formerly been termed "association" and what is now regarded by Longinescu as "molar concentration."

47. Electron distribution in the chlorine ion. G. G. HARVEY AND G. E. M. JAUNCEY, *Washington University, St. Louis.*—Jauncey and Claus (Phys. Rev. **31,** 717 and **32,** 12 (1928)) have obtained theoretical F values for the chlorine ion in rocksalt from the assumption of a Bohr model in which the Compton effect has been taken into account according to the method of Jauncey (Phys. Rev. **29,** 757 (1927)). These theoretical values were in fair agreement with the experimental values. It occurred to the writers to subject both the Jauncey and Claus theoretical F curve and the experimental F curve for chlorine to a Fourier analysis, thus obtaining a U curve. The U curves for different values of D, the grating space, calculated from the experimental F values are independent of the value of D used, being practically superposable. Such is decidedly not the case with the theoretical curves, the general shape changing as well as the peaks shifting. This seems to show that the Compton effect cannot be taken account of in the way proposed by Jauncey and supports the theoretical finding of Waller (Phil. Mag. **4,** 1228) and Wentzel (Zeits. f. Physik **43,** 1 and 779) that a Schroedinger charge density may be assumed for the atom and the Compton effect disregarded in calculating F values.

48. Temperature effect in diffuse scattering of x-rays from rocksalt. W. D. CLAUS, *Washington University, St. Louis. (Introduced by G. E. M. Jauncey.)*—According to Debye (Ann. d. Physik **43,** 49 (1914)), the intensity of x-rays diffusely scattered in a direction ϕ from a crystal should be equal to that scattered from an amorphous substance, multiplied by the temperature factor $(1-e^{-M})$. Experiments by Jauncey (Phys. Rev. **20,** 421 (1922)) show that the intensity scattered is proportional to $\sin(\phi-\theta)/\{\sin(\phi-\theta)+\sin\theta\}$ as predicted, where θ is the crystal angle. Experiments are at present being conducted to test the temperature effect. In the temperature range 295° to 135°K, a decrease of approximately 50 percent in intensity is to be expected (depending on slightly different assumptions used in calculation) for $\phi=30°$ and 60°. Results to date indicate a decrease of not more than 5 percent, in no wise comparable to the expected effect.

49. Spectroscopic analysis of scattered x-rays. J. A. BEARDEN, *Johns Hopkins University.*—Davis and his collaborators using a double crystal spectrometer have found a fine structure in the spectra of scattered x-rays. Several investigators using a single crystal method have failed to find any fine structure. The present experiment is a repetition of Davis' experiment using a double crystal spectrometer on the unmodified line. Greater scattered x-ray intensity has been obtained by using a line focus tube and placing the scattering blocks of aluminum and graphite about 5 mm from the focal spot. Two wave-lengths were used, the $K_{\alpha_1}K_{\alpha_2}$ line of silver and the $K_{\alpha_1}K_{\alpha_2}$ line of copper. The capacity of the electrometer system was about 12 cm and the sensitivity of the electrometer 20,000 scale dimension per volt. No fine structure lines of one tenth the intensity of the K_{α_2} line have been observed. Chemical analysis of the scattering blocks showed no trace of copper or silver as an impurity. Measurements have also been made on the Compton shift which agree very closely with the equation $\delta\lambda=(h/mc)(1-\cos\theta)$.

50. Scattering of x-rays and the distribution of electrons in helium. ARTHUR H. COMPTON. *University of Chicago.*—An analysis of the theory of scattering of x-rays by monatomic gases makes it possible to express the probable distribution of the electrons in the atom as a Fourier integral. To evaluate this integral it is necessary to know the intensity of scattering of x-rays of known wave-length at different angles. With data recently obtained by C. S. Barrett the distribution of electrons in atoms of helium gas is thus determined. This distribution agrees

satisfactorily with that calculated by Pauling from wave-mechanics but differs by more than the experimental error from that predicted from Bohr's theory.

51. A direct-reading two-crystal spectrometer for x-rays. F. K. RICHTMYER, S. W. BARNES AND E. RAMBERG. *Cornell University.*—The two-crystal spectrometer developed by Bergen Davis and others provides a means of obtaining monochromatic x-rays of high intensity. Such a spectrometer, reading wave-lengths directly in angstroms, has been constructed, using the principle described by Nicholas (J.O.S.A. & R.S.I. **14,** 61, Jan. 1927) for the single crystal instrument. Details of construction and adjustment are described; and sources of error are discussed. The instrument is capable of absolute measurement of wave-lengths, with very high precision.

52. A vacuum spectrograph for the precision measurement of x-rays of long wave-length. CARL E. HOWE, *Oberlin College.*—The spectrograph has four unique features which make it fitted for precision measurements. (1) A slit system, consisting of five slits each one thousandth of an inch wide, excludes optical light and gives excellent collimation of the x-rays. (2) An x-ray tube with interchangeable targets, mounted on a micrometer slide enables the focal spot to be readily lined up with the fixed slit system. (3) A universal grating support permits the plane grating to be set at any desired angle and to be removed in vacuo from the path of the x-rays without disturbing any adjustments. (4) A set of two parallel plate holders at a fixed and known distance apart, placed at right angles to the slit system, permits accurate measurements of angles from the lines recorded on the two plates at different distances from the grating. The slit system and grating support are mounted as one unit which may be completely removed from the rest of the spectrograph for the purpose of making adjustments.

53. An instrument for high-voltage x-ray spectrography and radiography. FREDERICK SILLERS, JR., *Follansbee Bros. Co.* (*Introduced by Wheeler P. Davey*).—The increasing application of the x-ray diffraction method of crystal analysis to the study of materials of construction has led to the desire, in certain fields, for a more rapid method of obtaining results. Such a method may involve the adoption of higher voltages than are now in general use for this type of work. An instrument suitable for use with these higher voltages (in the neighborhood of 200 kv) will be described. The instrument consists essentially of a lead-lined drum equipped with four pin-hole or slit diffractometers, as well as an opening for radiographic exposures. It is adapted to a standard 200 kv installation employing a Coolidge tube. The instrument is so designed that comparable intensities of x-rays at all four diffractometers are available, rendering practicable the comparison of different patterns. Through the use of the present instrument x-ray spectrograms, by direct transmission, of coarse-grained polycrystalline material; e.g., high-silicon sheet steel about 0.02 in. thick for electrical uses, may be obtained in less than an hour. If radiographs are desired during the course of any study, they may be obtained by rotating the tube 90° on its axis.

Points to be discussed deal with strained materials, intensifying screens, optimum voltage, intensity variations, and radiography of fine effects.

54. The dielectric constants of aqueous KCl solutions. ALLEN ASTIN, *National Research Fellow, The Johns Hopkins University.*—Probable causes of the many discrepancies in existing data on the dielectric constants of aqueous electrolyte solutions have been determined and methods of either eliminating them or correcting for them worked out. It is shown that by use of a voltage resonance method, (Jezewski, Zeits. f. Physik **48,** 123 (1928)); (Kneikamp, Zeits. f. Physik **51,** 95 (1928)); (Lattey and Gatty, Phil. Mag. **7,** 985 (1929)) and (Astin, Phys. Rev. **34,** 300 (1929)), the necessary corrections are considerably simplified. The voltage resonance curve is also shown to be symmetrical, regardless of the amount of damping. The corrected results show that the dielectric constants of aqueous KCl solutions from concentrations of 0.00025N to 0.01N are no different from that of water, at least within the limit of error of the measurements. The probable error of the corrected results is 2 parts in 1000 at 0.001N. and 6 parts in 100 at 0.01N. The uncorrected results show an apparent decrease of the dielectric constant similar to that reported by most other observers. The magnitude of this apparent

decrease may be varied by changing either the frequency, the size of the test condenser or the dimensions of the leads. The lowering of the dielectric constant in solutions which was predicted by Hückel (Phys. Zeits. **26**, 93 (1925)) is much smaller than any reported experimentally and is too small to be detected with the limit of error reported here. Frequency employed is 1.8×10^6.

55. Time lag in changes of electrical properties of rubber with temperature and pressure. ARNOLD H. SCOTT, *Bureau of Standards.*—When the temperature of rubber is suddenly (within five minutes) changed from one value to another, the electrical properties do not at once assume their final values. Two hours or more may be required for the dielectric constant, power factor, and resistivity to become constant. Part of the data for one specimen are given in the following table:

Time after specimen reaches 150°C (125° Change) Minutes	Dielectric Constant	Power Factor Percent	Equilibrium Temp. corresponding to dielectric constant and power factor
3	3.07	2.96	107°C
15	3.52	7.83	120
25	3.83	8.87	128
63	4.32	6.22	144
155*	4.39	4.42	150

* (Equilibrium)

This time lag was studied with specimens of several compositions from soft to hard rubber following temperature changes varying in amount from 75 to 125°C. Data on the time lag with pressure were obtained on only one specimen using pressures between 1 and 700 atmospheres. Twenty-four hours were required for the electrical properties to become constant.

56. Changes in the specific resistance of aluminum. G. E. DAVIS AND GILBERT GREENWOOD, *University of Rochester.*—Measurements on aluminum wires confirm previous investigations concerning the increase of specific resistance with cold-working. Tammann attempted to explain this increase by assuming particle orientation. Such orientation has since been found in the fibrous texture of drawn wires. This explanation, however, requires anisotropic electrical properties of the metallic crystals. Such anisotropy is most unlikely in cubically crystallized aluminum. Furthermore aluminum wires, annealed until the increase in specific resistance is lost, show distinctly fibrous texture. The increase in specific resistance has sometimes been ascribed to lattice distortions caused by the stresses of cold working. v. Arkel investigated such distortions by the effects produced in Debye-Scherrer photographs. The α-lines in such photographs are actually doublets ($K\alpha_1$ and $K\alpha_2$), the sharpness of resolution of which decreases with increasing lattice distortion. Aluminum, completely annealed or cold-worked to different degrees, always shows a sharp resolution of these doublets. Distortions of the v. Arkel type cannot, therefore, be responsible for the increased resistance. Dehlinger discussed distortions extending throughout very minute regions of the lattice—possibly only along the surfaces of the particles. Such distortions would not cause a decrease in the sharpness of the doublets, and might be responsible for the increased specific resistance.

57. Contact resistance and microphonic action. F. S. GOUCHER, *Bell Telephone Laboratories.*—An experimental study of single contacts between granules of microphone carbon, the contact forces being of the order of 1 dyne. For established contacts Ohm's Law is obeyed up to 0.1 volt. The resistance decreases with increase of temperature, the temperature coefficient of resistance being of the same order of magnitude as that of solid carbon wires produced by a heat treatment which is similar to that used in the preparation of the microphone carbon.

Above 0.1 volt (up to 1.0 volt) there are departures from Ohm's Law which can be accounted for by the theory of contact temperature as a function of voltage when a reasonable value of the Wiedemann Franz ratio for carbon is assumed. The conclusion is that the conducting portions of such contacts are carbon to carbon. The temperature coefficient of resistance of a contact varies in a reproducible, but non-systematic manner as the resistance is changed in a reversible resistance force cycle. This shows that new surfaces having coefficients different from the average value are inserted into or removed from the circuit during the cycle.

58. A theory of the resistance of alloys. L. W. NORDHEIM, *University of Goettingen* (*Introduced by Alpheus W. Smith.*)—According to the new (Sommerfeld-Houston-Block) theory of metallic conductivity any resistance in a conductor is due to an imperfection of the crystal lattice. Thus the ordinary resistance is due to the heat motion of the atomic ions, and, therefore, is essentially dependent on the temperature, and vanishes at the absolute zero point. In alloys an additional disturbance is introduced because of the irregular distribution of the constituents. This disturbance can be calculated and gives the additional resistance, which is independent of temperature. Most facts about the resistance of alloys are easily explained by this picture. Formulae are given for the simplest cases, which are in good agreement with experiment.

59. Shot effect of the emission from oxide cathodes. H. N. KOZANOWSKI (*Introduced by N. H. Williams, University of Michigan.*)—Fluctuations in the electron space current from barium-strontium oxide cathodes at low accelerating potentials are many times as large as those observed in the case of currents from metallic emitters. When space charge is obliterated by the use of high accelerating potentials, the true value of the electronic charge, as predicted by Schottky, is obtained. The results indicate that at low accelerating potentials, positive ions leave the emitter, and travel into the space charge region under the action of the reverse space charge field. Due to the low mobility of the positive ion, large groups of electrons are affected by each positive ion, thus causing large, sudden variations in the space charge. A tube containing a tungsten filament and a Kunsmann emitter surrounded by a cylindrical collector gives the normal shot effect when only the tungsten is heated. The same abnormally high values observed with the barium-strontium emitter are obtained with this tube with a low accelerating potential when positive ions emitted from the Kunsmann emitter interact with the electron space charge around the tungsten filament. Even in this case, the true value of the electronic charge is obtained when the space current is temperature limited.

60. Effect of positive ion shot effect on space charge limited electron currents. LLOYD P. SMITH, *Cornell University.*—A transcendental equation has been derived which relates the electron current between two parallel plane electrodes (one of which is a hot cathode emitting positive ions as well as electrons, and the other is a collecting electrode at a potential positive with respect to the cathode) to the total positive ion emission as well as the difference of potential between the electrodes, their distance apart, etc. Curves have been plotted which give the electron current to the collecting electrode as a function of the total positive ion current at various collector voltages. From such relations, the variation in the electron current produced by statistical variations in the positive ion emission can be obtained. Such variations are large compared to the ordinary shot effect. This is to be expected since a positive ion moves relatively slowly through the space charge region liberating a group of electrons during one transit. From the curves it is possible to obtain the difference of potenial between the electrodes, at which the fluctuations of the positive ion current produce the greatest variation in the electron current.

61. Studies of abnormal shot effect in gaseous discharges. JOHN S. DONAL, JR., *University of Michigan.* (*Introduced by N. H. Williams.*)—Space charge limited electron currents from hot filaments have been found to exhibit extremely abnormal fluctuations when the tube contained argon gas. The abnormality is due to the release of groups of electrons from the space charge region by the positive argon ions. A detailed study has been made of the variation of the abnormal fluctuations with the field, filament temperature and gas pressure, the results

have obvious application to the elimination of extraneous noises in vacuum tubes. Positive ion currents of the order of one microampere have been obtained from tungsten filaments undergoing attack by oxygen. These ions, when trapped in the minimum of potential surrounding a hot cathode, produce very abnormal fluctuations in space charge limited electron currents. An expression for the resulting shot voltage has been developed, which permits the calculation of the average anode current increase due to each positive ion, and the average time of life of the ions in the space charge region. When the positive ions are accelerated to a cold cathode, an abnormal shot voltage is obtained which is unusual in being independent of the positive ion current.

62. Effect of adsorbed thorium on the thermionic emission from tungsten. WALTER H. BRATTAIN, *Bell Telephone Laboratories.*—The thermionic emission from a tungsten ribbon filament on which thorium was deposited, has been investigated. The thorium was derived from a thorium filament placed parallel to one face of the tungsten ribbon. For each successive equal amount of thorium deposited, the corresponding increase in the logarithm of the emission, for a given temperature of the tungsten ribbon, was smaller and smaller until the emission reached a maximum. Continued deposition of thorium caused the emission to decrease and finally approach a stationary value. Further investigation indicated that migration of the thorium to the back side of the tungsten ribbon took place at an appreciable rate at 1500°K. At approximately 1800°K. there was definite evidence of diffusion of thorium into the tungsten ribbon. At higher temperatures, the thorium evaporated from the tungsten surface.

63. The ion-grid theory of the decrease in work function for composite surfaces. J. A. BECKER, *Bell Telephone Laboratories.*—When electropositive atoms are adsorbed on electronegative surfaces, some of the atoms are ionized. These adsorbed ions act like a positively charged grid very close to the cathode. For a large plane surface, this ionic grid produces strong fields close to the surface but only small fields at larger distances. As a result, the work function is reduced by $4\pi\sigma l$ and the emission current saturates as well as it does for clean surfaces. σ = charge per cm^2; l = distance of ions above surface. In most experiments, however, the surface consists of irregularly oriented facets or else the ions form clusters due to the presence of electronegative gases. In these cases the distribution of the fields is greatly dependent upon the size of the facets or clusters. Computation shows that for small applied fields, the work function is decreased by a *fraction* of $4\pi\sigma l$. As the applied field increases, this fraction increases and the emission current increases much more rapidly than for clean surfaces. For large fields, the current saturates as well as or even better than for clean surfaces. Numerous experimental observations are accounted for by the finite extent of the ion-grid.

64. Grid glow tube relays. D. D. KNOWLES AND S. P. SASHOFF, *Westinghouse Elec. & Mfg. Co., East Pittsburgh.*—The name Grid Glow Tubes applies to a line of gaseous discharge glow and arc tubes, the breakdown of which is controlled by means of a grid. They are, then, essentially relays having a discontinuous grid-voltage plate-current characteristic These tubes are made in two general types: tubes with a cold cathode and tubes in which the negative electrode is a hot filament—the characteristics of both types being similar. Grid Glow Tubes have been made in sizes ranging from a few milliamperes of plate current up to several hundred amperes. They can be filled with one of the inert gases neon, argon, or helium or with mercury vapor. A study of the behavior of these devices must necessarily include that of the type of circuit in which they are to be used. A series of curves plotted for both a.c. and d.c. voltages on the plate, a.c. and d.c. grid bias and various self biasing schemes are given. The effect of phase shift between the grid and plate voltages when alternating current is used is also illustrated.

65. The radioactivity of Stone Mountain. JAMES A. HOOTMAN AND W. S. NELMS, *Emory University.*—The radioactive content of the waters which issue from the base of the unique geological formation known as Stone Mountain (Georgia) was determined. Tests were made of a number of large springs well distributed around the base of the mountain, and of other shallower sources above and below the 1000 foot level. The method employed was the Schmidt

Shaking Method, in which a known volume of water is thoroughly shaken with a known volume of air in a closed container. The resulting mixture of air and radium emanation is then pumped into an electroscope, and the rate of fall of the leaf is a measure of the radioactivity of the water. The electroscopes were calibrated by means of the Duane and Laborde formula, and corrections were made for temperature and pressure. This method has been shown by Ramsey to have an accuracy of about 3%. A majority of the springs tested were highly radioactive, the value for the highest being $15{,}980\times10^{-12}$ Curies per litre. This value is nearly twice the maximum reported by Boltwood for fourty-four radioactive springs, and more than half as large as the maximum reported by Lester for one-hundred-seventy-eight mineral waters of Colorado.

66. The measurement of the intensity of gamma rays of radium in r-units. OTTO GLASSER AND V. B. SEITZ, *Cleveland Clinic Foundation.*—Determinations of the intensity dsitribution of gamma-rays were made under various experimental conditions with a condenser intensitometer previously described. By using small ionization chambers and a system unaffected by penetrating radiations the difficulties usually encountered in such measurements were greatly reduced. The intensities obtained are given in *r*-units.

67. Disintegration constant of actino-uranium and ratio of actinium to uranium. ALOIS F. KOVARIK, *Yale University.*—With data of Fenner-Piggot and of Aston for br ggerite, Karlhus, Norway, and also Aston's 206, 207, 208 line intensities in common lead mass spectrum in conjunction with my age formula (Phys. Soc., April 1929) amounts of common lead and AcD are calculated. AcD, uranium, and actinium: uranium ratio (3%) lead to $\lambda=2.5\times10^{-9}$ yr^{-1} or $T=2.7\times10^{8}$ yr. Boltwood's 8% (N. Car. uraninite), Hahn-Meitner's 3% (pitchblende) and others, including recent work of Wildish, indicate a variation of the ratio with age of mineral. Considerng actino-uranium an isotope of uranium initially in correct proportion to UI, the ratio should vary and 400 million years difference in the age of the minerals will bring Boltwood's and Hahn-Meitner's values into agreement. Furthermore, calculation of this ratio for the age of Keystone, S. D., uraninite (1462 million years) gives 0.6% and for Sinyaya Pala, Carelia, uraninite (1852 million years) gives 0.25%. The latter values receive a check if AcD is practically the only lead isotope left after subtracting RaG and ThD from the total. Broggerites and cleveites do not give such a check because considerable amount of common lead is present.

68. An attempt to detect deBroglie waves of hydrogen atoms. THOMAS H. JOHNSON, *Bartol Research Foundation.*—Earlier work on the reflection of atomic hydrogen from NaCl failed to reveal deBroglie wave diffraction patterns. This was not unexpected because of the low intensity of the specular reflection and the great intensity of the diffuse background, arising principally from the reemission of adsorbed atoms. Lithium fluoride presents a much more favorable opportunity for detecting the wave character of atomic hydrogen. The specular beam is very intense and there is no reemission of monatomic hydrogen. The MoO_3 detecting plate therefore records only elastically reflected atoms. First order surface-grating bands from the LiF lattice were expected with abrupt maxima separated from the specular beam by 20° to 30°. These bands were found, showing that the total number of atoms going into any one is certainly less than 5% of the number in the specular beam. If the crystal was heated to 600° C a diffuse band appeared extending asymmetrically to about 20° on either side of the the specular beam. With the crystal at room temperature this largely disappeared.

69. Satellites of electron diffraction beams. H. E. FARNSWORTH, *Brown University.*—While investigating electron diffraction by a copper crystal, for normal incidence on a (100) face, certain beams have been found which require a refractive index of unity. A search for other weak beams of this nature reveals a whole set of such beams which accompany the intense diffraction beams. In many cases these satellites are so close to the regular beams that they are not completely resolved, and hence are not observed by the usual method of measurement. In the (100) azimuth the satellites which accompany the 4 first-order beams below 325 volts all occur within 2 volts of the theoretical values for unit refractive index;

that of one second-order beam occurs within 11.9 volt; that of the other second-order beam is missing. In the (111) azimuth, the satellites of 3 first-order beams are within 2.7 volts of theoretical values; that of the other first-order beam below 325 volts is within 7.3 volts; those of 2 second-order beams are within 5 volts; that of the other second-order beam is within 19.5 volts; that of 1 third-order beam is within 5 volts. These satellites are as sharp in voltage and colatitude angle as the main diffraction beams, and are not confined to large colatitude angles. Hence they are not due to a two-dimensional surface grating. The significance of these diffraction beams is discussed.

70. The capture of electrons by alpha-particles. A. H. BARNES, BERGEN DAVIS AND H. L. HULL, *Columbia University.*—Abstract of this paper is withheld for revision by the authors.

71. Absorption of sodium vapor in the extreme ultraviolet. S. A. KORFF AND J. L. NICKERSON, *Princeton University.*—Employing a vacuum spectrograph, sodium vapor was examined for absorption in the region from 1300 to 300 Angstrom units, againt a background of many lines. Vapor pressures used ranged up to 1 mm of Hg. No broad absorption peaks were observed in this region. Extremely narrow peaks would not be distinguishable, however, by this test. This region includes the point at twice the series limit, or 1205.9 Angstrom units. In general, sodium vapor was found to be almost perfectly transparent to radiation in the observed range.

72. Most probable 1930 value of the electron and related constants. R. A. MILLIKAN, *California Institute of Technology.*—This paper discusses, in the light of Zwicky's results on the block structure of crystals, the reliability of old and new measurements on the relations of e and h, and by combining experimental and theoretical considerations assigns most probable 1930 values to these constants.

73. The nature of cosmic radiation. L. F. CURTISS, *Washington, D. C.*—Two Geiger-Müller tube counters placed vertically above each other show, in addition to accidentals, coincidences which have been ascribed to cosmic rays. Absorption experiments by Bothe and Kohlhörster indicate that these rays are corpuscular. The author has made observations with the poles of a large electromagnet between two counters, recording the number of coincidences with and without the magnetic field. With the field used of 7000 gauss over an area 24 cm in diameter, a parallel beam of 10^9 volt electrons which passes through the upper counter would be deflected sufficiently just to miss the lower counter in spite of the fact that the $H\rho$ for such electrons is approximately 3×10^6. Since the radiation is actually diffuse with a maximum in the vertical direction, using two counters one can expect only a slight decrease in the coincidences if they are caused by high-speed electrons. However, if they are due to ultra γ-rays, no such effect should be observable. Making the theoretical allowance for accidentals, a decrease of the order of 25% has been observed in the coincidences which may be attributed to cosmic radiation. This confirms the existence of a corpuscular radiation of very high energy.

74. The absorption of acetylene and ethylene in the near infrared. RICHARD M. BADGER, *California Institute of Technology. (Introduced by Richard C. Tolman).*—The absorption spectra of gaseous acetylene and ethylene have been investigated photographically in the region 6800A–9200A. In the case of acetylene a band with very sharp lines, and showing marked intensity alternation was found, with center at about 7886A. It resembles a band found by Levin and Meyer at 3.0μ, of which it is probably a harmonic, but shows strong convergence on the short wave length side indicating a considerable increase in the average moment of inertia due to oscillation. In the case of ethylene a band was found with center at about 8706A which apparently also shows convergence, but which has a rather complex structure. An investigation of the structure of these bands is in progress.

75. The effect of high pressure on the near infra-red absorption spectra of certain liquids. J. R. COLLINS, *Cornell University.*—The state of polymerization of liquids composed of polar molecules is supposed to depend on the temperature, pressure, etc. The near infra-red absorption

bands of these substances, which are due to molecular vibrations, should be affected by changes in the state of polymerization, and hence also by changes in the temperature, etc. Experiments have shown that changes in the temperature changed the spectral position and intensity of absorption bands of water and certain alcohols, while the bands of benzene, a nonpolar substance, were unaffected by changes of temperature. The present experiments are measurements of the absorption of water, methyl alcohol, and iso amyl alcohol as examples of polar substances, and of toluene as a nonpolar substance, when these substances were subjected to pressures up to 5000 atmospheres. The pressure chamber was designed by P. W. Bridgeman and the measurements were made in the Jefferson Laboratory at Harvard University. No change was found in the position of any of the absorption bands studied. The conclusion is made that, in this pressure range, the state of polymerization does not depend on the pressure.

76. Bismuth-black and its applications. A. H. PFUND, *Johns Hopkins University.*—If a bit of bismuth be evaporated from a spiral of incandescent tungsten wire in a space evacuated to a pressure of about 0.25 mm of mercury, the bismuth is deposited as an intensely black film. For visible light, the diffuse reflectivity of "bismuth-black" is but one sixth that of camphor black. Tests have shown that bismuth-black films which are opaque to visible light, transmit and reflect at normal incidence, less than 1% of infra-red radiation out as far as 13μ. It was decided to use this new material on the receiving areas of delicate thermopiles, radiometer vanes, etc. Quite apart from the blackness and small heat capacity of bismuth-black, a further advantage is gained because of the circumstance that the most delicate surfaces may be blackened without the least danger of harming them. Because of the fineness of the particles, films of bismuth-black on plate glass reflect specularly at grazing incidence. Films which are rough at all angles of incidence may be produced by depositing, first, an extremely thin (grayish) film of soot from burning camphor upon which the bismuth-black is subsequently thrown down. It appears that the soot particles act as centers of condensation and, as a result, the bismuth-black is built up in the form of minute pyramids. Delicate surface bolometer's were made by forming a layer of nitrocellulose so thin as to show first-order Newton's colors. Upon this film was deposited a highly reflecting film of bismuth. The best attainable vacuum—less than 10^{-4} mm Hg—was required. This film was an excellent conductor for electricity. Air was then admitted so as to raise the pressure to 0.25 mm and the absorbing film of bismuth-black was thrown down. This general mode of procedure is being applied to the construction of thermopiles.

77. The effect of aberrations in limiting the resolving power of infra-red spectrometers. R. BOWLING BARNES AND A. H. PFUND, *Johns Hopkins University.*—Because of the increasing demand for high dispersion infra-red measurements, it seems timely to call attention to some of the difficulties which arise when very small "slit-widths" are used, and to a method of overcoming them. In the usual spectrometer, concave mirrors must be used off the optic axis, and unless these are parabolized along the proper axes, noticeable aberrations are present. Due to astigmatism and coma the slit image is broad and accompanied by a diffuse wing. If the eye is placed behind S_2, and the grating viewed in monochromatic light only a small portion of it will be illuminated, the jaws of the narrow slit having blocked out the light from some parts. One then, never gets the advantage of the full aperture, and the spectrum used is very impure. By a method somewhat similar to that described by Pfund (J.O.S.A., April 1927), spherical mirrors of aperture $f \cdot 4$ can be used along the optic axis, and to full advantage. The radiation, after falling upon each of the spherical mirrors, M_1 and M_3, is reflected along the axis to the plane mirrors, M_2 and M_4 respectively. These mirrors, containing oversized slits at their centers, are placed just in front of the slits S_1 and S_2, and are inclined to the optic axes at the desired angles. With this arrangement the eye looking through S_2, sees the entire grating filled with light no matter how narrow the slits are made. This is a necessary result if one wishes to work with very small "slit-widths".

78. On the theory of the Brownian motion. L. S. ORNSTEIN, *University of Utrecht, Holland* AND G. E. UHLENBECK, *University of Michigan.*—Using a method first indicated by Ornstein (Proc. Acad. Amst. **21**, 96, 1917) the mean values of *all* the powers of the velocity

u and the displacement s of a free particle in Brownian motion are calculated. It is shown that $u-u_0\exp(-\beta t)$ and $s-u_0/\beta[1-\exp(-\beta t)]$ where u_0 is the initial velocity and β the friction coefficient divided by the mass of the particle, follow the normal Gaussian distribution law. For s this gives the exact frequency distribution corresponding to the exact formula for S^2 of Ornstein and Fürth. Discussion is given of the connection with the Fokker-Planck partial differential equation. By the method exact expressions are obtained for the square of the deviation of a harmonically bound particle in Brownian motion as a function of the time and the initial deviation. Here the periodic, aperiodic and overdamped cases have to be treated separately. In the last case, when β is much larger than the frequency and for values of $t>\beta^{-1}$, the formula takes the form of that previously given by Smoluchowski.

79. A test of the Dalton-Gibbs law of partial pressures. LOUIS J. GILLESPIE. *Massachusetts Institute of Technology* (*Introduced by F. G. Keyes.*)—According to Gibbs' formulation the pressure of a gaseous mixture equals the sum of the partial pressures, $P=\Sigma_1 p_1$, when p_1 is conceived as the pressure of pure gas 1 that would just prevent the gas 1 in the mixture from escaping through a membrane permeable to it alone. This can be shown equivalent to the statement: The "density" (or concentration) of a gas is the same at equilibrium on either side of a membrane permeable to it alone. Examination of the data of Larson and Black and of Lurie and Gillespie shows the following: (1) The mole fraction of ammonia mixed with 3:1 hydrogen-nitrogen mixture at temperatures from -20 to $+20°$ C, and of ammonia mixed with nitrogen at 45°, is greater than that calculated from the Gibbs formulation, by an amount that increases with the pressure at low pressures (50 atm. plus). (2) In the case of the hydrogen-nitrogen mixtures the difference appears to pass through a maximum at 100-300 atmospheres. (3) The difference may reach 25% of the observed mole fraction. (4) Considered as a possible basis for the thermodynamic treatment of gaseous equilibrium the Gibbs formulation must be regarded as approximate, like its analog, the fugacity rule of Lewis and Randall.

80. A rational basis for the thermodynamic treatment of mixtures of real gases. JAMES A. BEATTIE, *Massachusetts Institute of Technology.*—In the treatment of the thermodynamic properties of gas mixtures several assumptions are necessary. It is now found that two assumptions suffice: One relates to the isothermal variation of the energy of pure gases and the other to the isothermal variation of the ratio of the equilibrium pressure of a gas in a mixture to the total pressure multiplied by the mole fraction of the gas. From these two assumptions it can be shown that at infinitely low pressures the following relations hold for all real gases: (1) The laws of Boyle and Avogadro, (2) the energy, entropy, heat content and thermodynamic potentials of a mixture of gases are equal to the sums of the corresponding quantities for the component gases existing each by itself with the same value of its volume, temperature and chemical potential as in the gas mixture; (3) the energies and heat capacities of gases and gas mixtures are functions only of the temperature; (4) $pv=nRT$ for pure gases and $pv=\Sigma_1(n_1)RT$ for gas mixtures where T is thermodynamic temperature.

81. A thermodynamic theory of excitation of nerves. N. RASHEVSKY, *Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.*—In their ionic theory of nervous excitation, W. Nernst (Pflugers Archiv, **122**, 275, 1908) and A. V. Hill (Journal of Physiology, **40**, 190, 1910) considered the motion of ions near a membrane, correspondingly between two membranes. Though the last case, worked out mathematically by Hill, accounts for the general features of the experimental excitation time curve, it does not account, without additional hypothesis, for the fundamental fact that the rate of increase of the exciting current is of prime importance. In the present paper, it is first pointed out that the boundary conditions, used in the mathematical treatment of Hill, cannot correspond to physically real cases, and a modified treatment is considered. Furthermore, it is shown that not only the general shape of the excitation time curve, but also the dependence on the rate of change of the exciting current, can be accounted for by purely thermodynamical considerations, which do not involve any special hypothesis about the ionic mechanism of excitation, and are based on considerations of systems with several equilibria.

82. The energy of dissociation of normal Cd_2. J. G. WINANS AND R. ROLLEFSON, *University of Wisconsin.*—Kapuscinski and Jablonski (Zeits. f. Physik **57,** 692, 1929) give an interpretation of the Cd absorption flutings between λ2825 and 2590 which yields 1.0 volts for the dissociation energy of normal Cd_2. From an interpretation of the Cd absorption band at λ2212 Winans (Phil. Mag. **7,** 555, 1929) obtained 0.20 volts for this dissociation energy. Walter and Barrett found that cadmium vapor from which electronegative elements had been excluded failed to show the λ2825–2590 flutings but still gave the 2212 band in absorption. They attributed the flutings to impurities in the cadmium and the 2212 band to cadmium molecules. The value of the dissociation energy obtained from the flutings is therefore doubtful. Also one should not expect an energy of dissociation as high as one volt for molecules like Cd_2. Since cadmium is a closed shell atom, a molecule formed by the union of two unexcited Cd atoms must be held together by polarization forces only. That such forces are too small to account for a large energy of dissociation of Cd_2 is made very plausible by consideration of the fact that the alkaline earths and helium which have a similar electronic configuration show no molecular absorption. The work of Koernicke on Hg_2 indicates that the energy of dissociation of such molecules is of the order of 0.1 volts.

83. The composition of the interior of the earth. A. A. BLESS, *University of Florida.*—The high density of the whole earth as compared with the density of the crust is usually accounted for by the hypothesis that the core of the earth is composed of iron. This hypothesis is inadequate for a number of reasons, the chief of which is that it gives an iron content for the earth much too high compared with the abundance of this element in the sun or in other stellar bodies. Without introducing such a radical hypothesis the high density of the interior of the earth may be explained as being due to the ionization of the materials composing the core, the ionization being produced by the collision of atoms moving with the high velocity of thermal agitation. A temperature sufficient to cause ionization by collision would be reached at a depth of 2000 miles if the temperature gradient observed near the surface remains constant for this distance. At a comparatively short distance from the surface the high temperature would cause decomposition of molecules. The permanent gases so liberated would form an envelope around elements which are solid at ordinary temperatures, these elements forming the core. The ionization of the material of the core by decreasing the size of the atom, would increase the density sufficiently to account for the observed mass of the earth. The suggested distribution of the material gives the proper value for the moment of inertia of the earth, and is also in qualitative agreement with data concerning the propagation of seismic waves.

84. Striations and magnetic effect in electrodeless discharges. J. TYKOCINSKI-TYKOCINER AND JACOB KUNZ, *University of Illinois.*—Electrodeless tubes filled with H_2 (0.01 mm Hg) were placed in the field of a coil with high frequency currents (3000–12000 kc.) of constant amplitude. Striations appearing in pairs were observed. Their number decreases with current density. Moving a tube away from a flat spiral coil is equivalent to decreasing the density of the discharge current, consequently the number of striations increases. At a certain critical distance the striations pass through a transitory stage of irregular movements to and fro and disappear then altogether giving place to a uniform glow. Striations were also obtained with the axis of the tube directed perpendicularly to the axis of the exciting coil, showing that the striations are not necessarily connected with ring discharges. A magnetic field applied perpendicularly to the axis of the tube produces a rotational deflection of each striation clockwise and perpendicular to the direction of the magnetic field. This deflection may be interpreted by the Biot-Savart action of the magnetic field on the radial component of currents formed by carriers moving spirally with increasing radii around the axis of the tube and directed outward. A similar interpretation is applicable to striations produced by high frequency discharges in tubes supplied with inner or outer electrodes.

85. High frequency electrodeless discharge characteristics. OTTO STUHLMAN, JR., M. D. WHITAKER, M. L. BRAUN, *University of North Carolina.*—These discharges are classed as primarily due to electrostatic and to electromagnetic fields. Excitation by damped and by un-

damped frequencies are considered. The investigation involved the production of a glow. discharge in mercury vapor as a function of frequency, pressure, current, and visual intensity. With a predominant electrostatic excitation and damped frequencies no simple relation was found to exist between visual intensity of the discharge and pressure, current, or frequency. However, consistent irregularities, characteristic of the gas and the mode of excitation, were obtained. With continuous wave and predominant electromagnetic excitation the minimum currents necessary to initiate, and necessary to sustain, the glow discharge were investigated at pressure ranging from 0.1 to 2.0 mm. For each frequency there exists a critical pressure at which the current through the coil required to initiate the glow discharge, and the current required to sustain it, are at minimum values. The ratio of these two currents is not constant for all pressures, but generally increases with increase in pressure. A characteristic arc transition from spark discharge at high pressure to arc discharge at lower pressures, occurred near 0.025 mm.

86. Relative intensities of arc and spark lines of the electrodeless discharge in mercury vapor. O. P. HART AND O. STUHLMAN, JR., *University of North Carolina.*—Excitation of discharge took place in a 12.5 cm spherical bulb placed inside a helical coil 14.5×44 cm when the latter was supplied with damped high frequency current. Three sets of spectrograms were taken—(A) Radiation intensity as a function of pressure with frequency and potential constant. (B) Intensity as a function of frequency with potential and pressure constant. (C) Intensity as a function of potential with frequency and pressure constant. Spectrogram series (A) showed that as the pressure was decreased (0.026 to 0.0005 mm) the intensity of the arc lines increased, whereas the intensity of the spark lines decreased. Series (B) showed that as the frequency of the excitation current was increased the intensity of the arc lines increased. No spark lines were observed at low pressures (0.0002 mm). Series (C) showed that as the potential between the terminals of the coil was increased the intensity of the arc lines increased. No spark lines appeared at this pressure (0.0002 mm). At low pressure and with increasing potential the triplet 4358, 5460, 4047 first appeared followed by the singlets 5790, 4347, 3906 in order of decreasing intensities.

87. Time lags in spark discharges at high overvoltages. J. C. STREET, *University, Va.*—Further studies of the long time lags in dry filtered gases at high overvoltage, first reported by Beams and Street (Phys. Rev. **35,** 658 A), have been made. Surge potentials were applied and the time lags were measured by a comparison method. Several enclosed gaps were constructed and tested, care being taken to remove the residual ions. In each case for air, nitrogen or hydrogen at atmospheric pressure the lags remained longer than 10^{-6} sec. until fields of about 3×10^5 volts per cm were reached. With an increase to 3.3×10^5 volts per cm the lags became less than 5×10^{-8} sec. The magnitude of the field, at which the transition from long to short lags begins, is little affected by increase in pressure, amounting only to about 3.4×10^5 volts per cm at three atmospheres. On the other hand it is remarkably increased by a previous treatment consisting of discharges between the electrodes at reduced pressures in hydrogen. After this procedure, fields of 6×10^5 and 5×10^5 volts per cm for spherical electrodes of brass and steel respectively were required to produce lags shorter than 10^{-6} sec. Fields of the same order of magnitude as those just mentioned were required to produce a spark under the same circuital conditions in high vacuum between the same electrodes.

88. A direct measurement of the velocity of cathode rays. CHARLOTTE T. PERRY AND E. L. CHAFFEE.—The method used in this experiment makes no assumptions as to the law of deflection of moving electrons in magnetic and electric fields but measures the time of flight of the electrons directly in their passage over a distance of about 75 cm. Electrons are projected through a long tube by a potential E. In their journey they pass through two very localized alternating electric fields. These deflecting fields are produced by a very high frequency oscillator connected so that the fields are 180° out of phase. Only those electrons which pass when the fields are zero reach the end of the tube. The time required to travel the distance between fields is an even multiple of the half period of oscillation of the fields. The accuracy of determination of velocity is better than 0.1% and results are given for various driving voltages E.

89. The ionization of helium and neon by electron impact. PHILIP T. SMITH AND JOHN T. TATE, *University of Minnesota.*—The total positive ion current per electron per centimeter path has been measured as a function of the energy of the impacting electrons up to 3000 volts in neon and up to 4500 volts in helium, using a modified Jones type of apparatus (T. J. Jones, Phys. Rev. **29,** 822 (1927)). Both helium and neon exhibit well-defined maxima which occur at 110 and 170 volts respectively. The ratio of the positive ion current to the electron current per centimeter path reduced to 1 mm pressure and 0°C at the maxima was 1.256 for helium and 3.056 for neon. At 3000 volts the ratio was 0.172 for helium and 0.605 for neon. It was found that for energies from about 500 volts to 3000 volts the efficiency of ionization of neon is a linear function of $V^{-\frac{1}{2}}$, where V is the energy of the impacting electrons in volts. In helium the efficiency is a linear function of $V^{-1/2}$ from about 500 to 2000 volts. Beyond 2000 volts the efficiency approaches a linear function of V^{-1}. The empirical formula

$$3.383(V_0/V)^{1/2}\left[1-\exp\left(-\frac{54V_0}{V}\right)\right]^{1/2}\left[1-\exp\left(-\frac{V-V_0}{2.28V_0}\right)\right]$$

expresses the efficiency of ionization of helium, within the experimental error, from the ionization potential V_0 to 4500 volts. The above results were free from any effects due to secondary electrons, and were independent of the pressure, electron current, and the magnetic field.

90. The absorption coefficient for slow electrons in gases. C. E. NORMAND AND R. B. BRODE, *University of California.*—The absorption coefficients or the effective collision cross sections have been measured in H_2, He, Ne, A, N_2 and CO for velocities of the electrons from 0.5 to 400 volts. With a higher resolution of velocity a fine structure in the absorption coefficient curves has been found for all of these gases. At the lowest velocities, about 0.5 volts, all of the curves are rising with decreasing velocity. The minimums in the absorption coefficients occur between 0.5 and 1.2 volts for these gases. Ramsauer and Kolloth (Ann. d. Physik **4,** 91 (1930)) have reported minimums for He and A and none for the other gases. Their scale of velocity is, however, in disagreement with the velocities measured here, being 0.5 volts lower. When adjusted for this difference the data are in agreement.

91. Heating of a cathode by positive gas ions, and their "accommodation coefficient." C. C. VAN VOORHIS AND K. T. COMPTON, *Princeton University.*—Positive ions of helium, neon or argon were produced by a low voltage arc at low pressure and were made to bombard a spherical molybdenum collector with regulated velocities up to 140 volts. The resulting heating of the collector was measured by a thermal junction and found to be *considerably less* than the product of current by bombarding voltage. The problem was to account for the undetected remainder of the energy. Both calculations and experimental tests showed that this cannot possibly be explained as the result of part of the apparent ion current actually consisting of secondary electron emission or of ions losing energy at collisions with molecules. After making all such corrections, we are still forced to conclude that a fraction of the kinetic energy of the incident ions is carried away by ions (atoms) after neutralization. The fractions of their energies delivered to the cathode by the ions are the following "accommodation coefficients": He 0.4 to 0.5, Ne 0.7, A 0.8, which are strikingly similar to the gas kinetic values. There are a number of interesting applications of this discovery.

92. Angle and energy distribution of electrons rebounding from gaseous molecules. A. L. HUGHES AND J. H. MCMILLEN, *Washington University, St. Louis.*—The distribution of electrons rebounding at definite angles from gaseous molecules was investigated. An electrostatic re-focusing arrangement was used to analyse the energies of the electrons. In helium, it was possible to identify the following energy losses at several angles, 21.12, 22.97, and 23.62 volts for a primary electron beam of 100 volts, but not the 19.77 and 20.55 volt losses. The number of electrons, rebounding without loss of energy, was measured for different angles of rebound (7° to 80°) from argon, helium, and molecular hydrogen molecules, and for various energies (50 to 15) volts). In almost all cases, the number decreased rapidly as the angle in-

creased. The higher the energy of the electrons, the more rapidly did the number fall off with increasing angle. The steepness of the curves increases as we go from argon to helium to hydrogen for the slower electrons. For the faster electrons their curves are practically superposable.

93. An attempt to detect collisions between photons. G. E. M. JAUNCEY AND A. L. HUGHES, *Washington University, St. Louis.*—It has been shown that if two photons, of identical frequency, moving along paths making an angle of 120° with each other, collide, and produce one photon travelling forward along the line bisecting the 120° angle, and another photon traveling in the opposite direction, the frequency of the photon traveling forward must be 1.707 of the frequency of the original photons (Hughes and Jauncey, Phys. Rev. **33,** 290 (1929)). This suggested the following experiment. Two beams of sunlight (one suitably deflected by a mirror), filtered through red glass, were passed through lenses 10 inches in diameter, so that the beams, whose axes made an angle of 120° with each other, intersected at a common focus. As the diameter of the beams at the focus amounted to only 4 mm, great concentration of light was obtained. The point of intersection of the beams was examined through a green filter with the eye which had been rested in total darkness for periods up to an hour. No light was detected. It was estimated that if the photon has a cross section, effective for the type of collision here contemplated, it must be less than 10^{-11} cm.

94. On the principle of Huyghens. G. E. UHLENBECK, *University of Michigan.*—Attention is called to the general formula:

$$\int_0^\infty d\nu \int_{-\infty}^{+\infty} f(\xi) \sin \nu(x-\xi)\, d\xi = P \int_{-\infty}^{+\infty} \frac{f(\xi)}{x-\xi} d\xi$$

where P denotes Cauchy's principal value. An exact (not published) proof of this has been given by Droste, when $f(\xi)$ fulfills the Dirichlet conditions. One has to compare this with the Fourier's integral theorem:

$$\int_0^\infty d\nu \int_{-\infty}^{+\infty} f(\xi) \cos \nu(x-\xi) d\xi = \pi f(x).$$

By integrating the wave equation in n dimensions $(\partial^2/\partial t^2 - \Delta_n)\psi = 0$ with given initial values for ψ and $\partial\psi/\partial t$ according to the method of Fourier-Cauchy, one can show that the curious difference between the formula's (1) and (2) reflects the well-known fact that the principle of Huyghens is not valid in spaces with n even number of dimensions and valid in spaces with an odd number.

95. The Stark effect near the series limit. JANE DEWEY, *University of Rochester.*—The number and position of the lines appearing near the limit in a hydrogen-like spectrum have been investigated on the Bohr theory, extending the work of Robertson and the writer (Phys. Rev. **31,** 973 (1928)). From a study of the limiting cases, for which the complete equatian can be handled more easily than in the general case, it appears that only orbits with principal quantum number less than a given number (approximately $43/F^{1/4}$) are periodic in the presence of a field. The region in which both lines and continuous spectrum appear is due to the large displacement of the lines. The outer components of the last group of lines appearing in a field of 1 e.s.u. per centimeter are displaced 50 cm^{-1}. For small fields the position of all the lines is given correctly by the perturbation theory if the second order terms are taken into account, as lines for which the series would not converge do not appear. The large displacements and large number of lines which appear near the series limit in a field make it probable that the lines observed in discharges in this region are the central components of the group of lines having the same principal quantum numbers and that the other components are spread over the background by the stray fields necessarily present. The apparent sharpness of the lines is thus not a criterion for no spreading out of the lines and an experimental investigation of the effect would be very difficult as it would probably not be possible to maintain a field sufficiently constant to observe the higher series members distinct from one another.

96. Zeeman effect in the calcium hydride band spectra. WILLIAM W. WATSON AND WILLIAM BENDER, *Yale University.*—The Zeeman effect in the red CaH bands has been investigated at several field strengths to 30,000 gauss, with a dispersion of 2.1A per mm. For $K<7$ in the $^2\Sigma\rightarrow{}^2\Sigma$ system, the P_1 and R_1 lines (parallel S) are unaffected at all fields, while the P_2 and R_2 lines (anti-parallel S) mostly become diffuse doublets shading away from the no-field position. All P_1 and R_1 lines of higher K value have at low fields only a strong, broad component shifted to the red with the extreme edge at about $\Delta\nu_{norm}$, the breadth decreasing as K increases. At 30,000 gauss a broad weak violet component appears. The P_2 and R_2 lines with $K>8$ are merely broadened to the violet, the overall width being approximately $\Delta\nu_{norm}$. The lines of low K values in the $^2\Pi\rightarrow{}^2\Sigma$ band give field patterns as expected from Hill's theory. For $K>22$, the lines involving F_1 states rapidly broaden out, and for highest K values are of negligible intensity. The lines arising from F_2 levels, remain sharp and strong for all high rotational states, but shifted to the violet by about $1/2(\Delta\nu_{norm.})$ These effects can be explained by a consideration of the "rho-type" doubling involved.

97. Electro-optical modifications of light waves. L. H. STAUFFER, *University of California* (*Introduced by Ernest O. Lawrence.*)—Broadening of the satellites of the Hg green line λ5461 was observed when the light passed between the plates of a Kerr cell on which was impressed a varying E.M.F. having a frequency of 2×10^7 sec^{-1}. The E.M.F. was obtained by superposing the output of a vacuum tube oscillator upon a steady potential of about 7000 volts. The maximum oscillator voltage was about 5000 volts. With this voltage the fine structure of the Hg green line became so diffuse that two satellites having a separation of 0.045A were scarcely resolved by the Lummer-plate. The broadening was observed to increase rapidly with the oscillator voltage. The observed effect is predicted by the classical electromagnetic theory and constitutes a proof of the generalized Doppler principle. The high frequency voltage effects a rapid variation of the refractive index of the nitrobenzene in the Kerr cell which in turn produces a corresponding variation in optical path, giving the source a virtual velocity. The observed broadening is in agreement with the predictions of classical theory.

98. The electric double refraction in gases. J. W. BEAMS AND E. C. STEVENSON, *University of Virginia.*—A method for the study of the electric double refraction or Kerr effect in gases as a function of pressure has been devised. Light of known frequency was passed through a Nicol prism, between two parallel metal plates, through a second Nicol prism and into a photoelectric cell. The two Nicols and the metallic plates across which the electric potential was applied were inclosed in a heavy steel tube with glass ends. As a result, the Kerr effect in the gas could be studied at a few hundred atmospheres pressure without introducing errors due to strains in the windows. Intense electric fields could also be employed because of the large value of the dielectric strength of the gas at high pressures. The precision of the method was limited only by the precision with which the potential across the plates could be measured. The results indicate that in the case of CO_2 the Kerr constant per molecule does not change by as much as 2 percent between 15 and 45 atmospheres pressure at 21° C. An easily measurable Kerr effect was observed in O_2 and N_2 at 100 atmospheres pressure.

99. Spontaneous temperature changes accompanying magnetization in steel. W. B. ELLWOOD, *Columbia University.*—The purpose of this experiment is to determine the dissipation of energy accompanying magnetization in iron by observing the change in temperature of a test specimen produced by a change in the magnetizing force at consecutive intervals in a single cycle of magnetization. The test specimen is in the form of an ellipsoid consisting of 104 bars of #57 drill rod alternate with 104 similar copper rods arranged in coaxial concentric cylinders. One hundred and two thermocouples in series are constructed by connecting adjacent copper and steel bars with 3 mm lengths of constantan and copper wire. Adequate thermal insulation isolates the specimen from the magnetizing solenoid in which it is placed. A temperature change of 3×10^{-6} degrees Centigrade can be detected. The specimen is put in a cyclic magnetic state and allowed to come to thermal equilibrium. On traversing the hysteresis loop from +290 to +20 gauss, heat is evolved by the iron and is measured as an increase in temperature.

On further demagnetization from +20 to −6 gauss the iron cools suddenly. From −6 to −90 gauss, the iron heats most rapidly. Increase of the field to −290 gauss is accompanied by cooling of the iron. Temperature-magnetization curves for various other magnetic paths are described.

100. The propagation of large Barkhausen discontinuities along wires. K. J. SIXTUS AND L. TONKS, *General Electric Co.*—Preisach has shown that by applying increasing tension or torsion to a wire of nickel iron allloy, the Barkhausen discontinuities in magnetization become larger and larger. Finally, at a tension near to the elastic limit, a rectangular hysteresis loop is produced whose discontinuous change in magnetization includes 97 percent of the whole difference between positive and negative saturation. Langmuir suggested that this sudden change in magnetization starts at a nucleus from which it propagates along the wire. Investigation based on this view shows that the nucleus forms in a uniform field at a somewhat variable critical field strength, and at different points along the wire, depending apparently on uncontrolled factors. The nucleus can be made to form at a definite point, however, by applying locally a small additive field, and the discontinuity will then propagate into the uniform portion of the field, the strength of which can be smaller than the critical field strength. The velocity of propagation increases for a given sample with increasing field strength and tension. A 10% Ni−90% Fe wire of 0.038 cm diameter showed velocities up to 14000 cm sec^{-1}

101. The mobilities of ions in moist and dry air. JOHN ZELENY, *Yale University.*—Using the method recently described (Phys. Rev. **34,** 310, 1929) the distribution of mobilities of aged ions in *dry air* has been determined and the values for moist air remeasured because of a neglected correction. The dissymmetry in the distribution of mobilities around the most numerous kind noted in the previous paper for *negative ions* in moist air, was found more pronounced in air dried by calcium chloride. In air dried further by passage through coils and filters immersed in liquid air a second distinct group of negative ions constituting about 35 percent of the total number and having a peak mobility of about 1.45 cm/sec was partially resolved. Under the last conditions the positive ion distribution curve also shows some dissymmetry indicating a possible group with a peak mobility of about 1.5 cm/sec. The mobility of the ions at the main peak of the distribution curve *decreased* for *positive ions* from 1.36 cm/sec for air with a water content of about 2 mg/liter to 1.05 cm/sec for the driest air used. Under similar circumstances the mobility of the *negative ions increased* from 2.08 cm/sec to 2.45 cm/sec. The existence of the two groups of negative ions is ascribed to a difference in size of the ion clusters arising from a difference in constitution at or near their centers.

102. Restriking of short a.c. arcs. F. C. TODD AND T. E. BROWNE, JR., *Westinghouse Elec. and Mfg. Co., East Pittsburgh.*—The restriking after zero current of short a.c. arcs with melting electrodes and of rapidly moving arcs with cold electrodes was investigated with a cathode ray tube of the Braun type. Long exposure photographs and observations of the volt-ampere traces on the fluorescent screen show the effect of the electrode vapor on the magnitude and variation of the restriking voltage. Brass, copper, iron, tungsten, and carbon were used as hot electrodes. The restriking characteristics of rapidly moving cold electrode arcs are influenced by the condition of the electrodes, magnitude of the driving magnetic field, and rate of rise of the voltage after current zero.

103. Extinction of short a.c. arcs between brass electrodes. T. E. BROWNE, JR. AND F. C. TODD, *Westinghouse Elec. and Mfg. Co., East Pittsburgh.*—Results are given which show that the dielectric recovery after current zero of short, stationary, a.c. arcs between brass electrodes is similar to that of cold-electrode arcs previously investigated and described. These results also show that the rate of recovery of dielectric strength of hot-electrode arcs after a current zero may be greatly increased by reducing, within limits, the electrode separation. An explanation is suggested on the basis of ionic diffusion to the electrode surfaces and the deionizing action of blasts of metal vapor from the boiling electrodes.

104. Problems suggested by an uncertainty principle in acoustics. G. W. STEWART, *State University of Iowa.*—At the suggestion of Professor A. Landé the principle adopted is

$\Delta\nu \cdot \Delta t \sim 1$, where ν is the intrinsic frequency of an acoustic signal and Δt is its time duration. Applying this principle one finds that it is consistent with experiments on the change in ν in the vibrato and the failure to detect it by ear, with recorded tests on minimum perceptible differences in frequency, and with the minimal time for tone perception. The problems suggested by the principle are: (1) variations in Δt and $\Delta\nu$ by an artificial vibrato with aural observations of detectable $\Delta\nu$, (2) redetermination of minimum perceptible differences in frequency as dependent upon Δt and (3) an examination of Δt required for tone perception with varied values of $\Delta\nu$ required for so-called tone perception.

105. The dispersion formula and Raman effect for the symmetrical top. MORRIS MUSKAT, *Gulf Research Laboratory Pittsburgh.*—Schroedinger's theory of dispersion is applied to the symmetrical top. The dipole of the top is assumed to lie along the axis of symmetry, and the wave-length of the incident light to be large as compared with the dimensions of the top. An explicit expression is derived for the index of refraction of a gas composed of symmetrical tops, as a function of the frequency of the incident light. As the perturbed eigenfunction is a linear function of only three unperturbed eigenfunctions, the dispersion formula, for a given state, consists of only two terms. The moments for the Raman effect transitions for the symmetrical top are also computed. Simple closed expressions are obtained, again because of the simplicity of the perturbed eigenfunctions. The polarization of the Raman radiations is computed with the result that the unshifted lines are unpolarized, whereas for the shifted lines, $|m_z|^2/|m_x|^2 = 4/3$.

106. The measurement of the variation in intensity of the helium lines with voltage by means of selected filters and a photoelectric cell. PETER J. MULDER AND JOSEPH RAZEK, *University of Pennsylvania.*—A method has been developed by which the variationsin the intensity of individual spectrum lines can be measured without resolution through a spectroscope, making use of a photoelectric cell and the recording amplifier described by Razek and Mulder as part of their automatic spectrophotometer (other paper, this meeting). This method has its application in the spectrophotometry of weak sources. We have used the method to study the variation of intensity of helium arc lines with voltage. The deflection of the amplifier galvanometer with various filters of known transmission coefficients for the lines to be measured interposed successively in the beam is noted. Assuming that all the energy recorded is limited to n lines, and that n filters are used, n equations soluble for ϕ_s of the form $L_a = a_1\phi_1 + a_2\phi_2 + \cdots + a_n\phi_n$ can be written, where L_a is the total light intensity as recorded with filter a interposed, $a_1 \cdots a_n$ are the appropriate filter transmission coefficients, and $\phi_1 \cdots \phi_n$ are the intensities of the lines multiplied by a factor depending on the wave-length sensitivety of the cell. To increase accuracy, more filters may be used and a reduction made to n normal equations by Gauss' method. In our work the helium lines were treated in four groups to reduce computation. The results generally checked with those obtained independently by a direct method.

107. The polarization and the electric moment of tung oil. A. A. BLESS, *University of Florida.*—The dielectric constant of a solution of tung oil in benzene of different concentrations was measured for three frequencies 10^6, 4×10^5, 10^5, using an electrical resonance method. The molar polarization of the solutions was calculated by the aid of the Clausius-Mosotti relation. The molar polarization proved to be a linear function of the mole fraction of tung oil, showing that the interaction of the polar molecules is in this case negligible. The polarization of the pure oil was found to be—364 cc, giving an electric moment of 2.195 e.s. units. The values found are substantially the same for each of the three frequencies for which the electric constant was measured.

108. Methods of acoustic interferometry for the measurement of velocity and absorption of sound in gases. J. C. HUBBARD, *Johns Hopkins University.*—In the well known acoustic interferometer of Pierce (Proc. Am. Acad. **60,** 271, 1925) the piezoelectric plate serves at the same time as generator of electric and acoustic oscillations. In order to eliminate the crystal as an essential part of the power circuit and use it only as a source of sound waves, thus to secure greater adaptability to the study of sound velocity and absorption over a range of temperatures and pressures, the writer has applied the method of forced piezoelectric vibrations used in the

sonic interferometer for liquids developed in collaboration with Mr. A. L. Loomis (Phil. Mag. June, 1928; J.O.S.A., Oct. 1928). The audible beat note of two Hartley circuits is adjusted in unison with a tuning fork, one of the circuits being provided with a secondory coil connected to the electrodes of the piezoelectric plate of the interferometer system. Cyclic variation of beat note as the gas column is lengthened is compensated by a vernier condenser in the exciting circuit, from the readings of which the velocity and attenuation of the sound in the gas are deduced. Acknowledgment is made to the Rumford Fund of the American Academy of Arts and Sciences, and to Mr. A. L. Loomis for the use of quartz plates.

109. Independence of x-ray absorption on temperature. J. A. BEARDEN, *Johns Hopkins University.*—Measurements have been reported (Read, Phys. Rev. **27,** 373 and Phys. Rev. **28,** 898) which indicated a change in the absorption coefficient of x-rays with change in temperature of the absorbing screen. Due to the theoretical importance of this effect the measurements have been repeated with much higher precision than was obtained in the previous work. The present method consists in comparing the intensity transmitted by two screens, first with both screens at the same temperature (about 24°C) and then with one screen raised to a higher temperature while the other was retained at 24°C. It can be shown that the percent change due to the expansion of the hot screen should be equal to $2\alpha T\mu\chi$ where αT is the linear expansion of the metal, μ the linear absorption coefficient of the transmitted beam, and χ the thickness of the screen. By making χ and μ large the expected change due to expansion in the present experiments was equal to 10 to 18 percent at 600°C. Measurements with wave-lengths from 0.4A to 1.5A showed no change from the expected change due to expansion.

110. On the heat of formation of molecular oxygen. L. C. COPELAND (*National Research Fellow in Chemistry*) (*Introduced by E. C. Kemble, Harvard University.*)—Molecular oxygen at pressures of 0.1 mm to 0.4 mm has been dissociated by the electrodeless discharge. The percent dissociation in the flowing gas was determined from pressure measurements on the high pressure side of a set of small orifices, using Knudsen's formula. Palladium black freshly deposited on a platinum surface has been shown to cause total recombination. A calorimeter consisting of such a surface fastened to a Beckmann thermometer and calibrating resistance coil with Woods metal was used to measure the energy of recombination. It has also been shown that the palladium black surface, poisoned with mercury vapor, or a shiny platinum surface do not cause total recombination. Several preliminary experiments have been made with about twenty-five percent dissociation at a rate of flow of 0.75 cc per minute.

111. On the mechanism of very absorbable radiation emitted by compressed crystalline substances under high potentials. ISAY A. BALINKIN, *University of Cincinnati* (*Introduced by S. J. M. Allen.*)— Following the work of Reboul, the emission from specially designed "radiating cells" was studied photographically. Powdered alum with the average size of the grains 0.0032 in. was subjected to a pressure of 300 kg/cm^2 in an atmosphere of 55% relative humidity. Under a potential difference of 5000 volts the emission from the cell was completely absorbed by celluloid, $t=0.13$ mm, and only partially absorbed by cellophane, $t=0.02$ mm. This corresponds to a range between very soft x-rays and short ultraviolet. A similar effect on the photographic film can be obtained by passing a spark discharge in an electrostatic field of about 1000 volts per centimeter in which the negative and positive ions are separated and then drawn into a recombination chamber. A Bunsen flame as an ionizing agent under the same circumstances, produces the same effect. The mechanism of the radiation emitted by the "radiating cell" under high potentials is explained by the external recombination of the ions which were produced in the interstices of the compressed crystalline substance. The wave-length of the emitted radiation corresponds to the ionization potentials of oxygen and nitrogen as given by the relation, $h\nu = Ve$. For a value of 14 volts, $\lambda = 900$A which agrees with the results given by the experiment.

112. A 21 ft. vacuum spectrograph for intensity measurements in the Schumann region. GEORGE R. HARRISON, *Stanford University.*—A 21 ft. concave grating ruled by Wood with 15,000 lines per inch and having a very bright first order has been mounted in vacuum for use in the Schumann region. The case consists of a 20 ft. vanadium steel tube of 16 inch internal

diameter, closed with tinned bronze castings. Three oil pumps exhaust this volume of 863 liters to 0.01 mm pressure in two hours; four large steel condensation pumps using n-dibutyl phthalate trapped with CO_2 lower the pressure to less than 10^{-4} mm in three more hours after. 50 hours of outgassing with the pumps off. The camera box holds 4 x 16 inch plates or films, recording at one setting a range of 900A with a dispersion of 2.7A per mm. Thirty exposures to different sources can be made without destroying the vacuum. The instrument, designed particularly for making intensity measurements on multiplets of multiply ionized atoms using the photometric methods developed by Leighton and the author for the Schumann region, has only been used to photograph the region 2200–1300A thus far; the strength of the spectrum indicates that 1000A should be reached without difficulty

113. Photographic record of the first order diffraction of hydrogen atoms by a lithium fluoride crystal. THOMAS H. JOHNSON, *Bartol Research Foundation*.—A beam of hydrogen atoms was reflected from a cleaved surface of a crystal of lithium fluoride at an angle of incidence of 30°. The plane of incidence made an angle of 45° with the cleavage edges of the crystal. In addition to the specularly reflected beam, first order beams appeared on the MoO_{12} detecting plates having the positions calculated from the wave-length $\lambda = h/mv$ and from the grating spacing of the rows of similar ions.

114. Double crystal spectra of scattered x-rays. NEWELL S. GINGRICH, *University of Chicago*.—To get high scattered intensity, two molydenum metal x-ray tubes of small diameter were used with a graphite scattering block between them. A total current of 95 m.a. at 50 k.v. was used. The effective scattering angle was about 109 degrees. Successive spectra taken in the neighborhood of the $K\alpha$ lines are not identical, since the experimental error is relatively large when measuring weak ionization currents. Nevertheless it can be said from the spectra obtained that the intensity of any fine structure line in the unmodified spectrum is probably not greater than 10 or 15 percent that of the $K\alpha$ line. The spectrum of the modified $K\alpha$ lines is observed at the position calculated from the equation $\delta\lambda = 0.0243\ (1-\cos\phi)A$. No evidence is found of fine structure lines in the modified spectrum as reported by Davis and Purks.

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